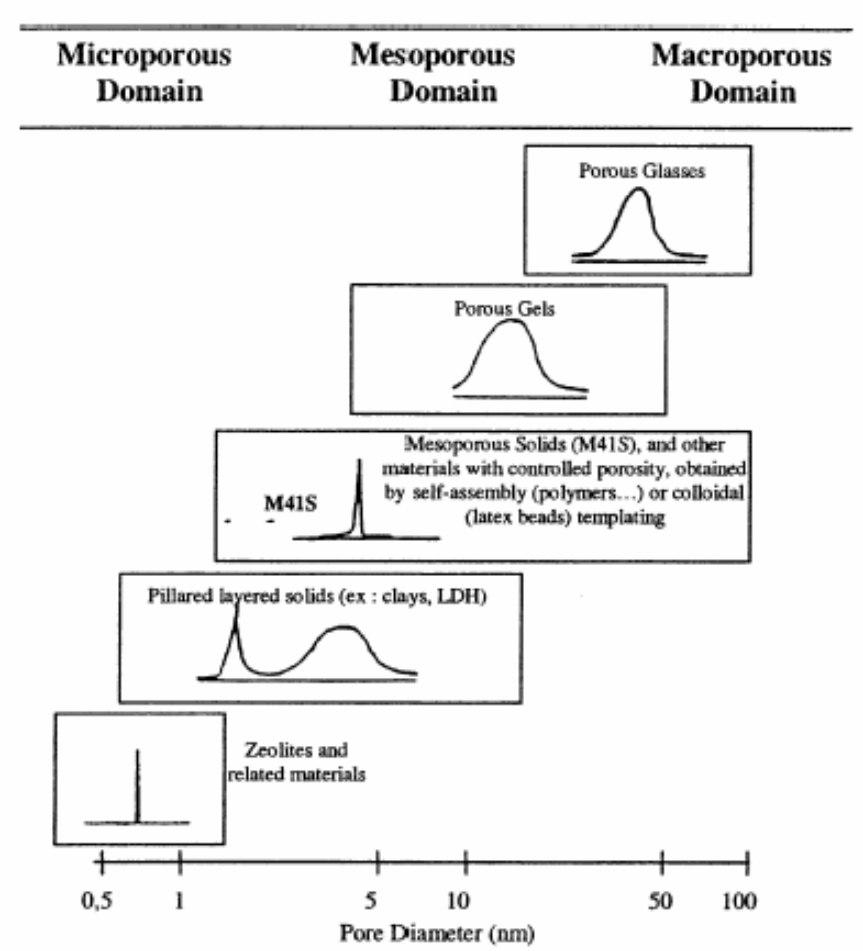
Mesoporous Materials

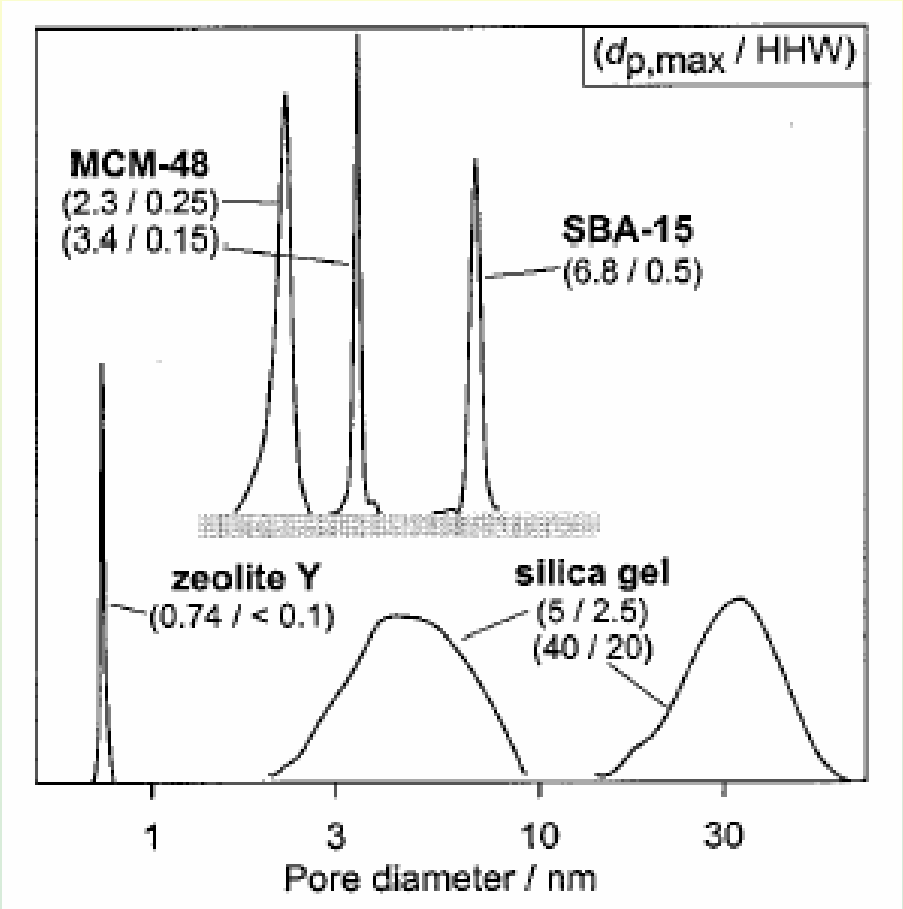
Amorphous, disordered - silica xerogels

Ordered, amorphous walls

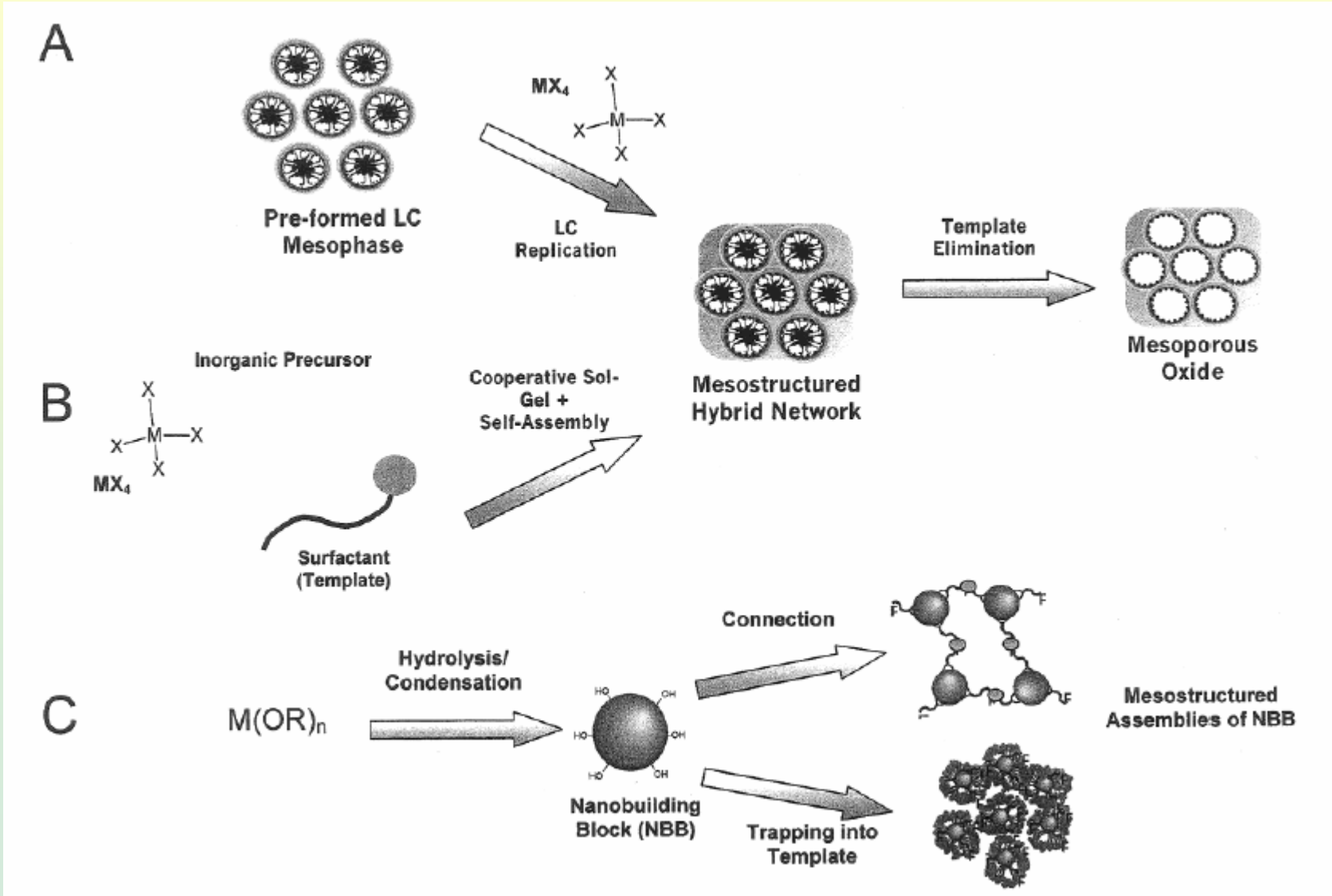
Pore diameter, ***d*** [nm]	Material	Example
$d > 50$	Macroporous	Aerogels
$2 < d < 50$	Mesoporous	Xerogels
$d < 2$	Microporous	Zeolites

Pore size distribution





Mesostructure Assembly



Mesoporous Materials

MMS mesoporous molecular sieves

MCM-n Mobil Composition of Matter

M41S

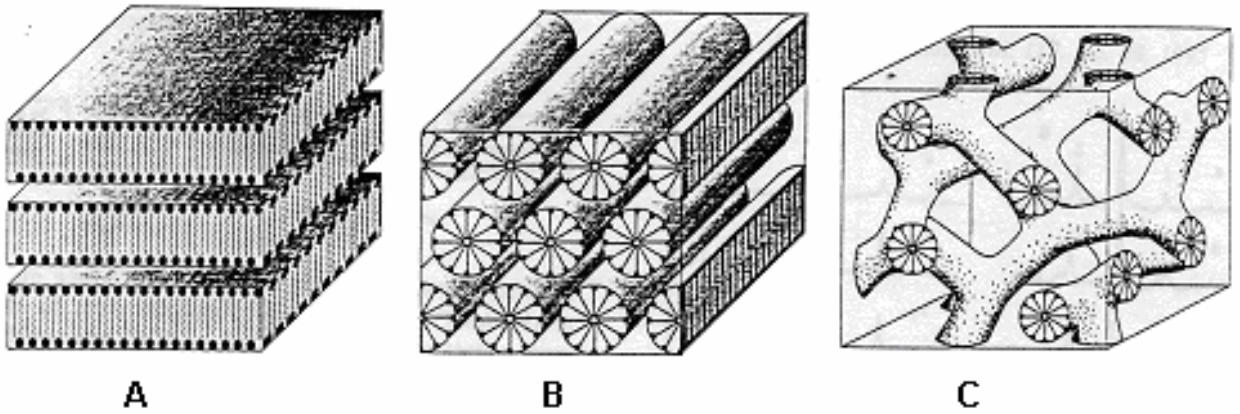
Discovered 1992

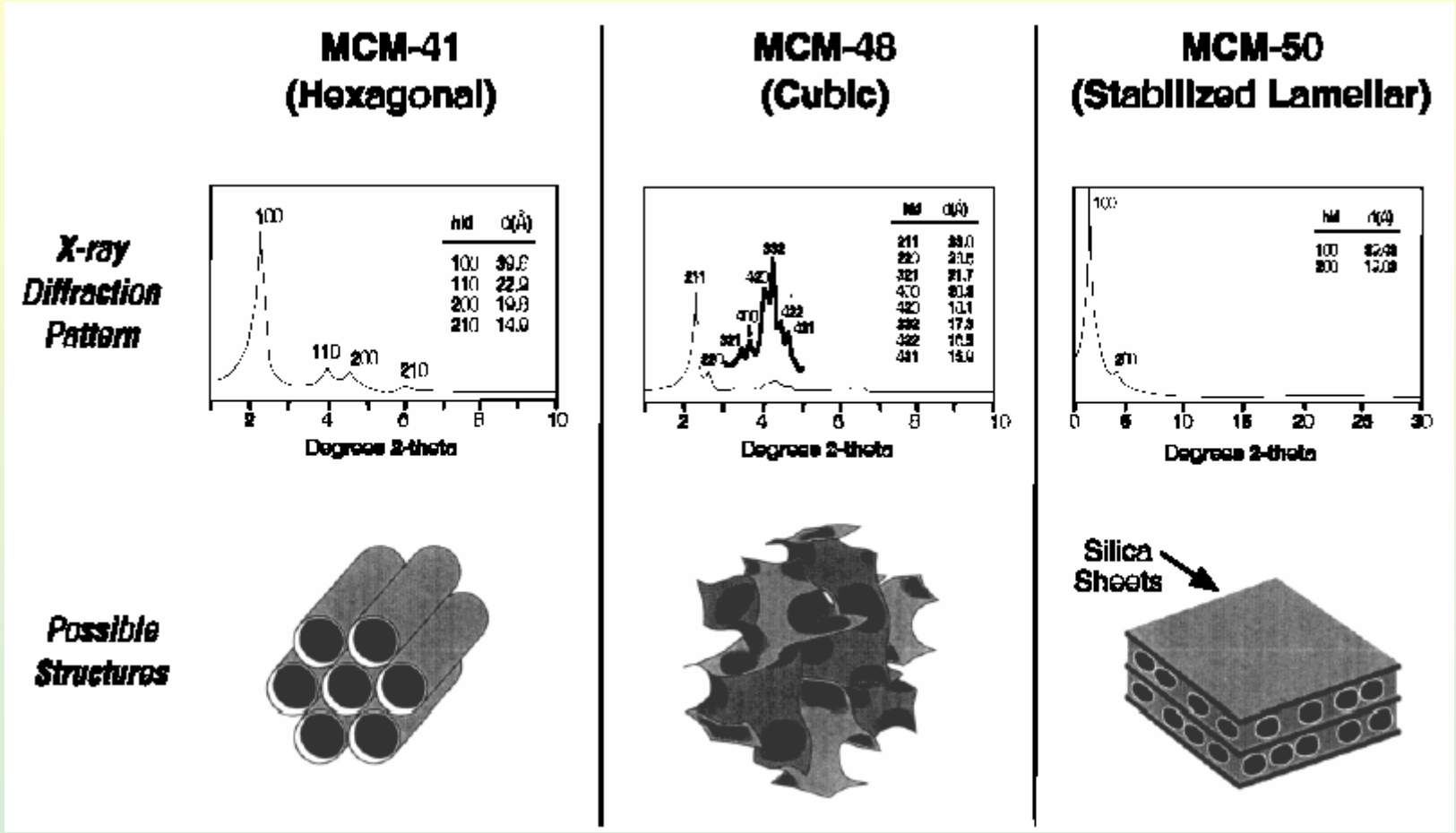
A - lamellar MCM-50

B - hexagonal MCM-41

C - cubic MCM-48

Inverse hexagonal




MCM-41
(Hexagonal)
MCM-48
(Cubic)
MCM-50
(Stabilized Lamellar)
X-ray
Diffraction
Pattern
Possible
Structures
Degrees 2-theta
Silica
Sheets

Supramolecular templating

Surfactants - amphiphilic molecules, polar (head group)and nonpolar (chain, tail) part

lyophilic, lyophobic

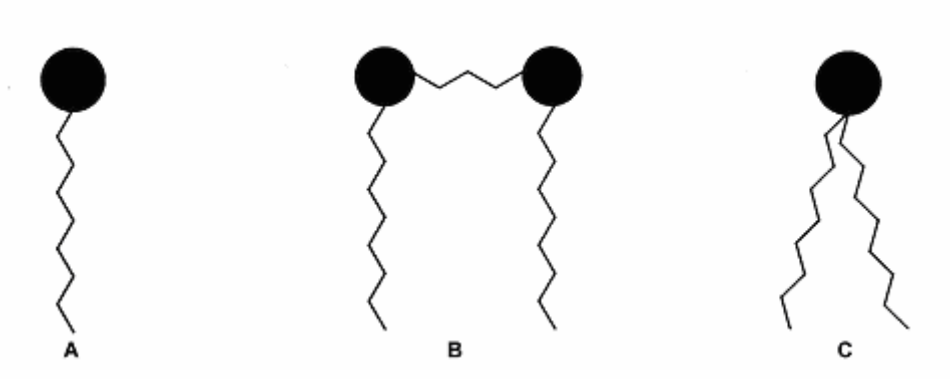
Ionic surfactants, cationic, anionic, zwitterionic

Nonionic amines, polyethyleneoxides

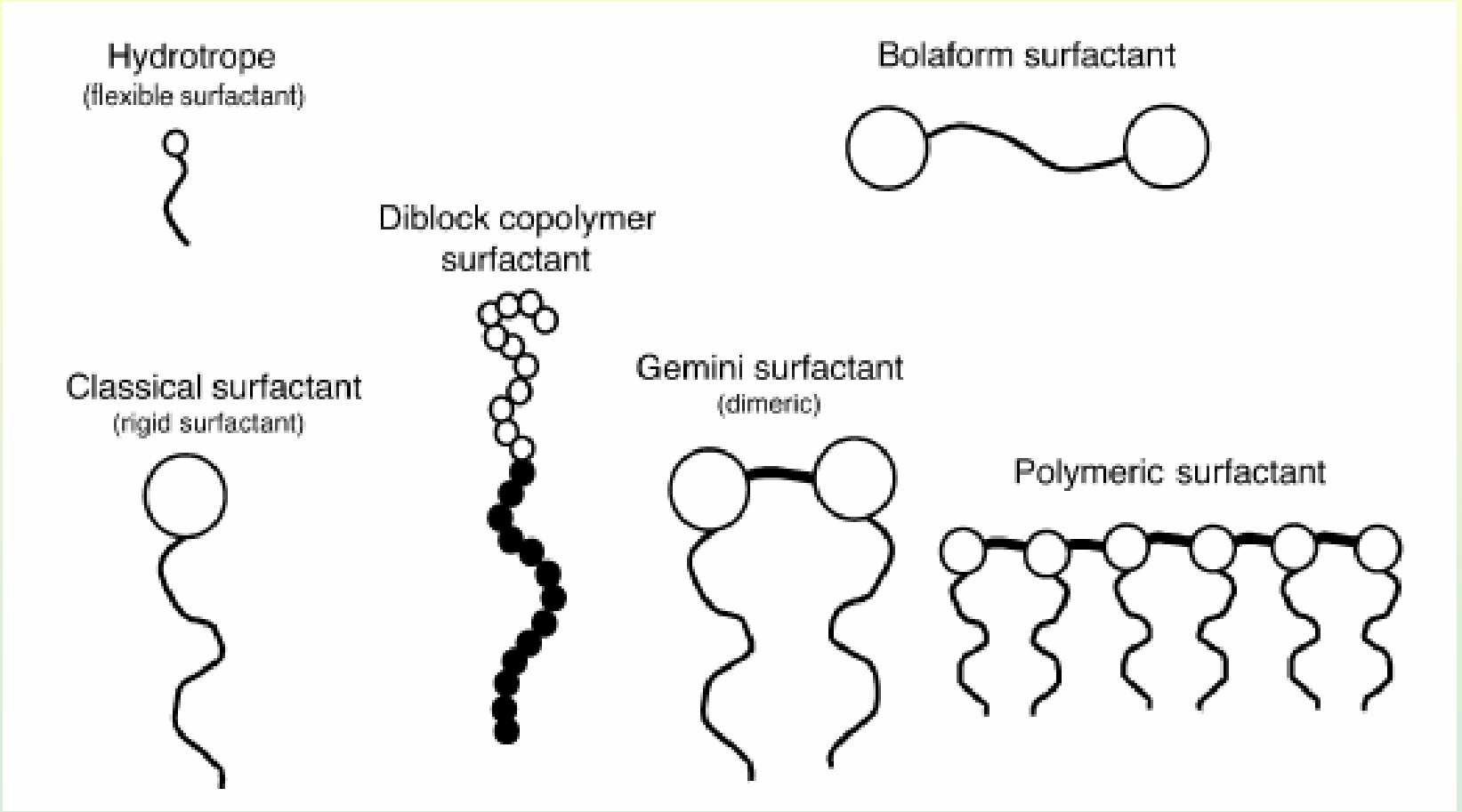
A - normal surfactant molecule

B - gemini

C - swallow tail



Surfactants



Surfactants

Anionic

- ***sulfates*:** $C_nH_{2n+1}OSO_3^-Na^+$
- ***sulfonates*:** $C_nH_{2n+1}SO_3H$
- ***phosphates*:** $C_nH_{2n+1}OPO_3H_2$
- ***carboxylates*:** $C_nH_{2n+1}COOH$

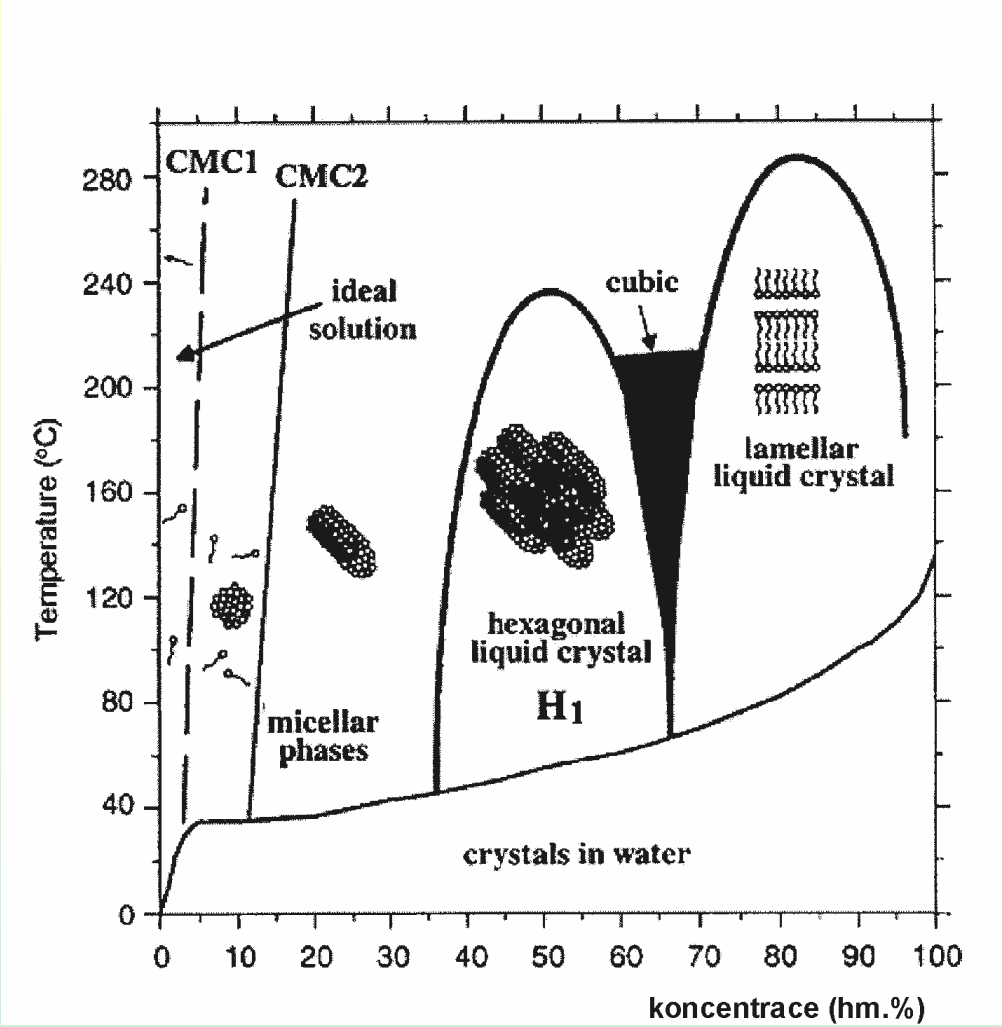
Cationic

- ***alkylammonium salts*:** $C_nH_{2n+1}(CH_3)_3NX$ X = OH, Cl, Br, HSO_4
- ***dialkylammonium salts*:** $(C_{16}H_{33})_2(CH_3)_2N^+Br^-$

Noionic

- ***primary amines*:** $C_nH_{2n+1}NH_2$
- ***polyethyleneoxides*:** $HO(CH_2CH_2O)_nH$

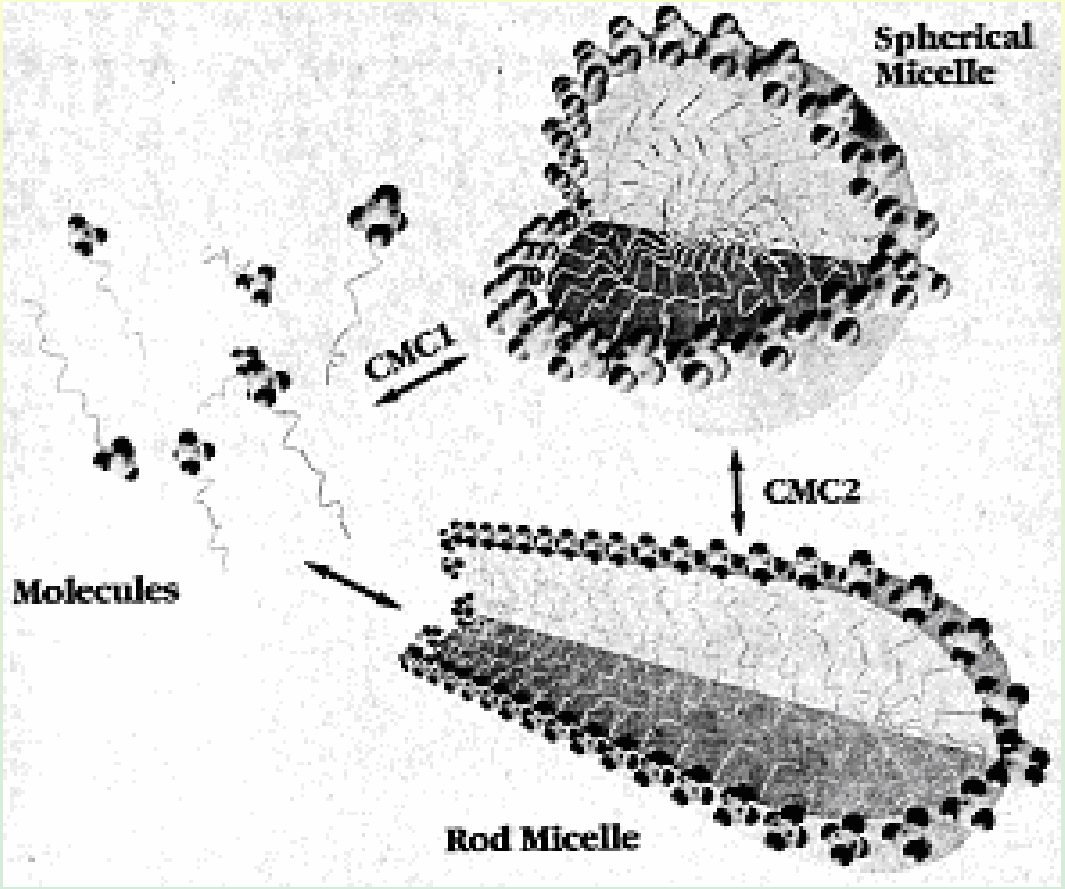
Supramolecular templating



Phase diagram of C_{16}TMABr

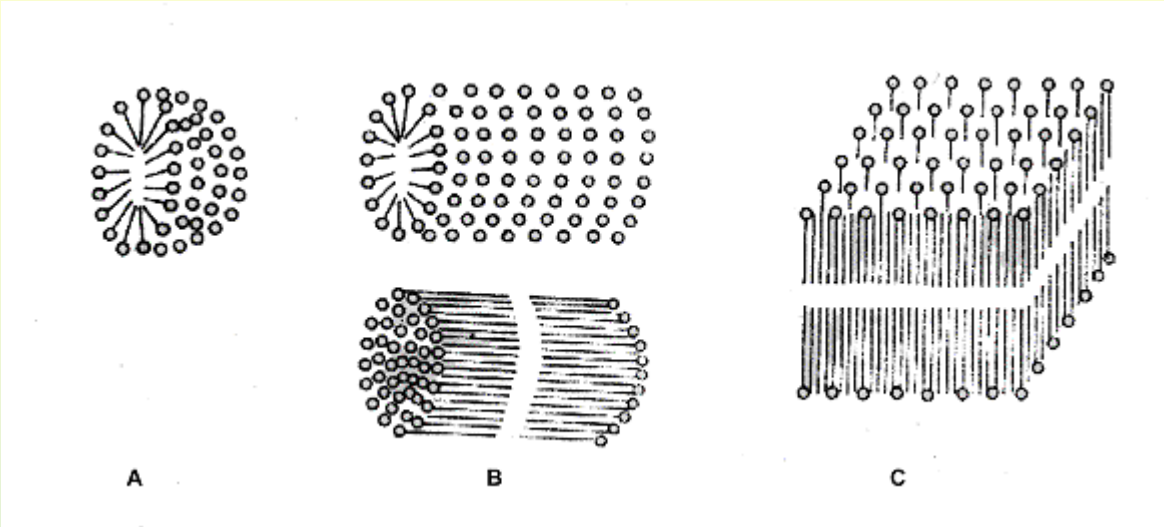
CMC = critical micelle conc.

Micelles - Supramolecular Templates



Micellar shapes

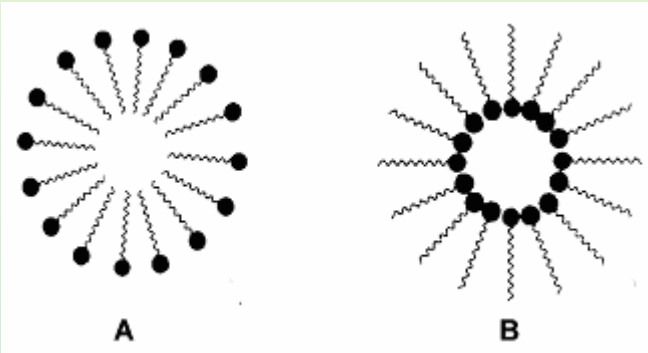
A -spherical, B - rod-like, C - lamellar



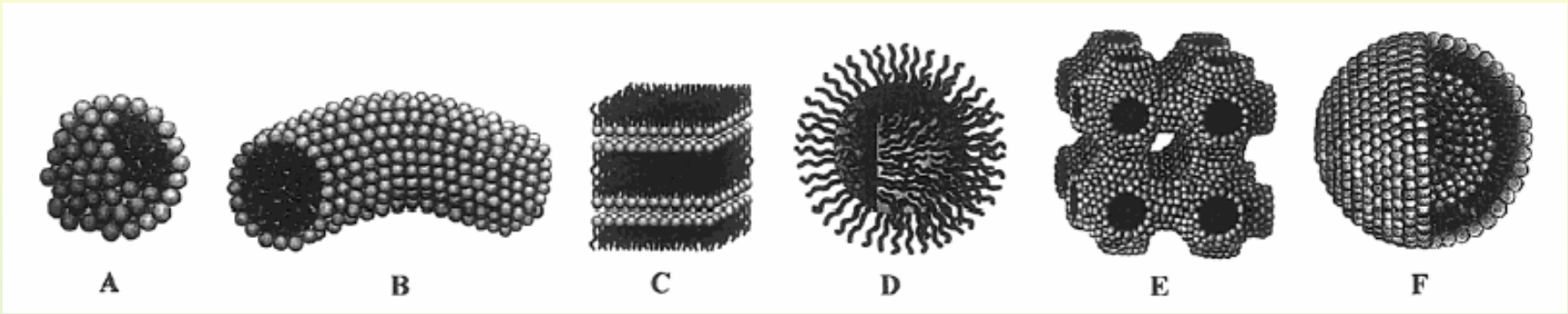
Micelles in media

A - normal, in polar solvent, H_2O

B - inverse, in nonpolar solvent, organics



Micellar shapes



Micellar structures

A) sphere, B) cylinder, C) planar bilayer,
D) reverse micelles, E) bicontinuous phase, F) liposomes).

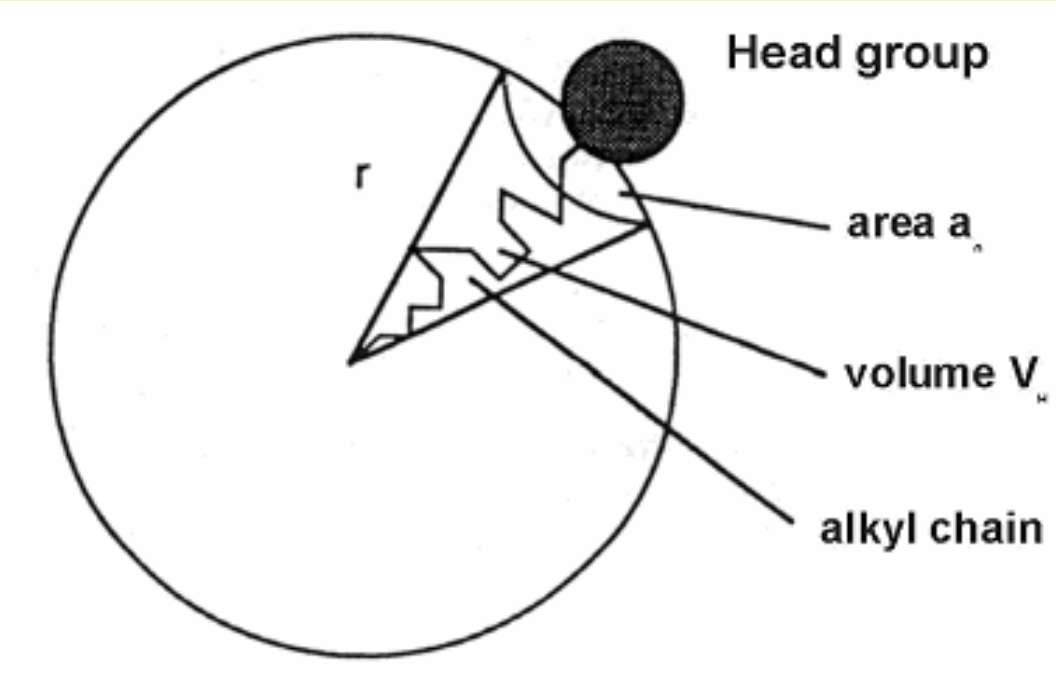
Critical packing parameter – CPP

$$CPP = V_H / a_0 l_c$$

V_H volume of the hydrophobic part, a_0 surface area of the hydrophilic part, l_c critical chain length:

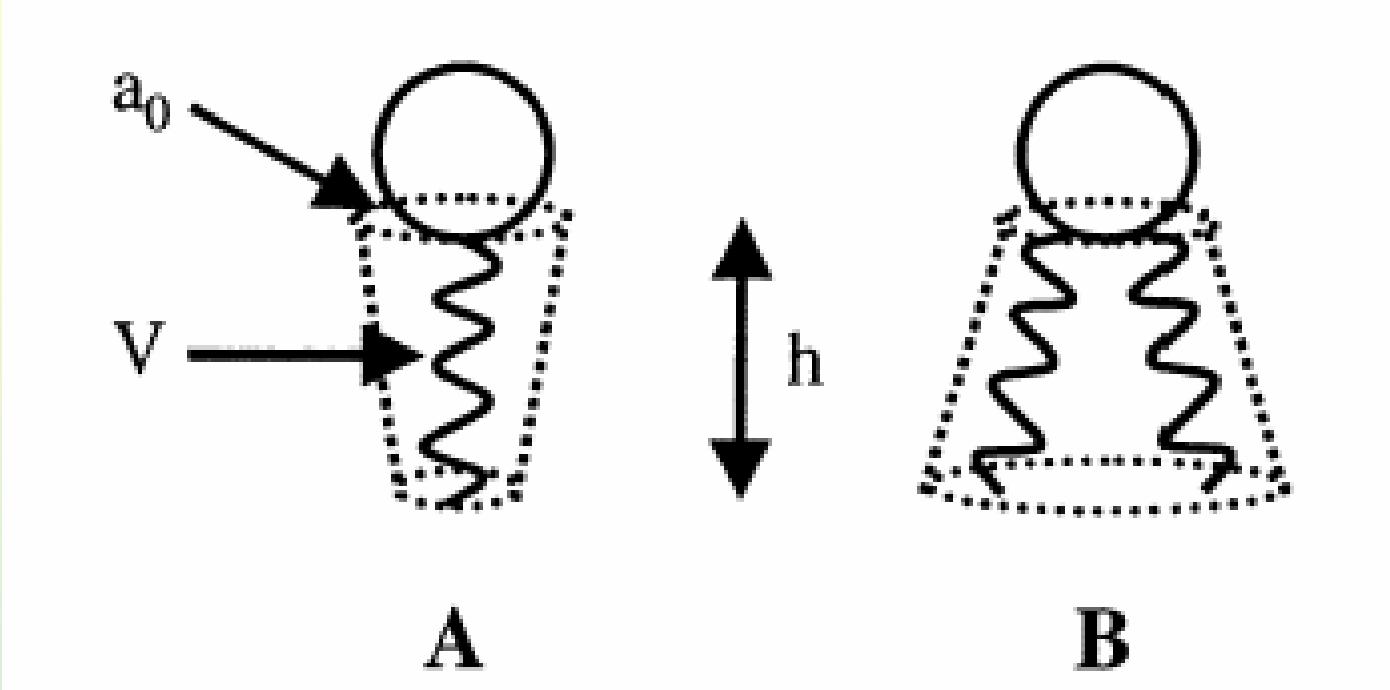
$$l_c \leq 1.5 + 1.265\ n \quad [Å]$$

n number of carbon atoms. l_c depends on the chain shape.



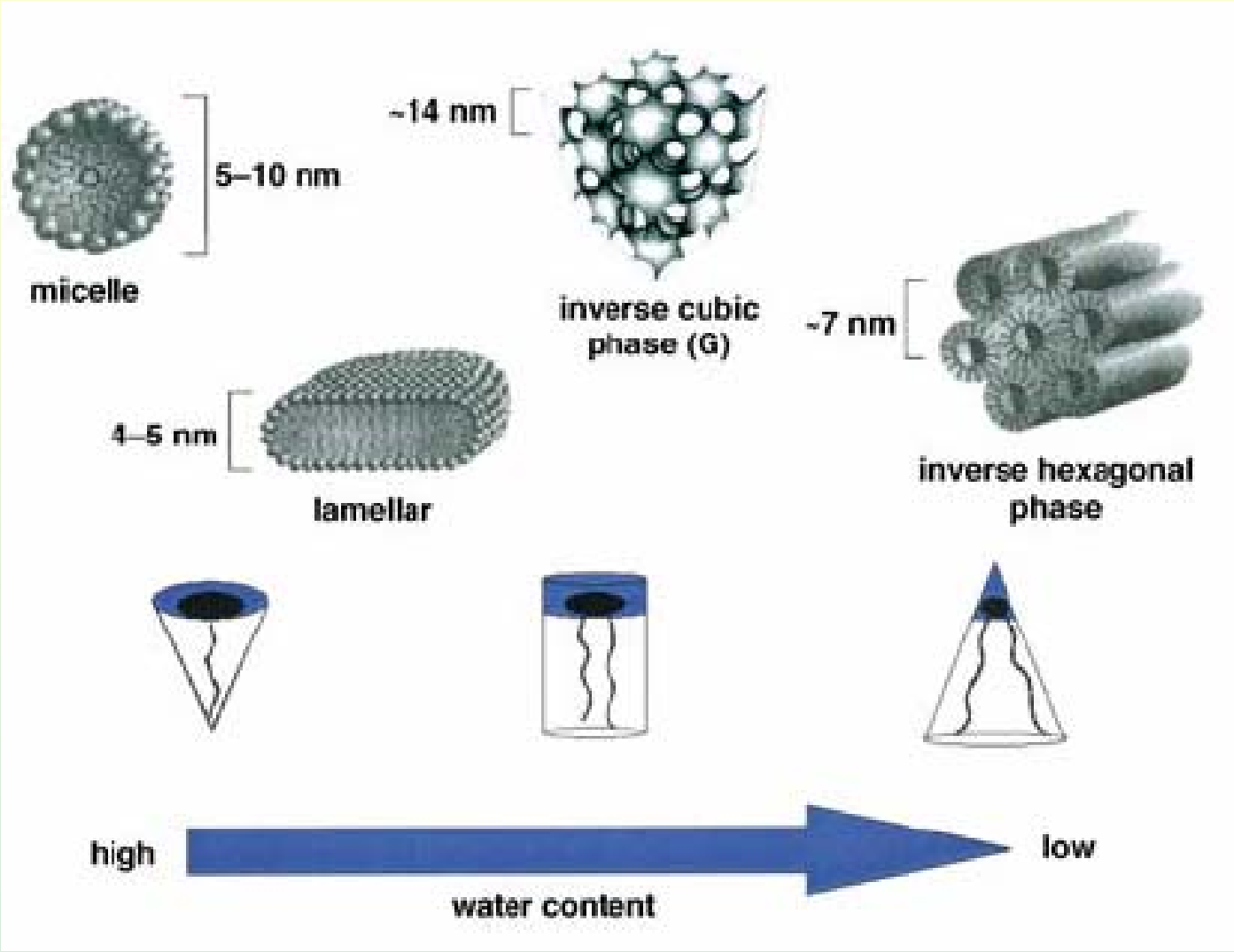
CPP	surfactant	micelle shape
< 0.33	linear chain, large head	spherical
0.33 - 0.5	linear chain, small head	cylindrical
0.5 - 1.0	two chains, large head	bilayers

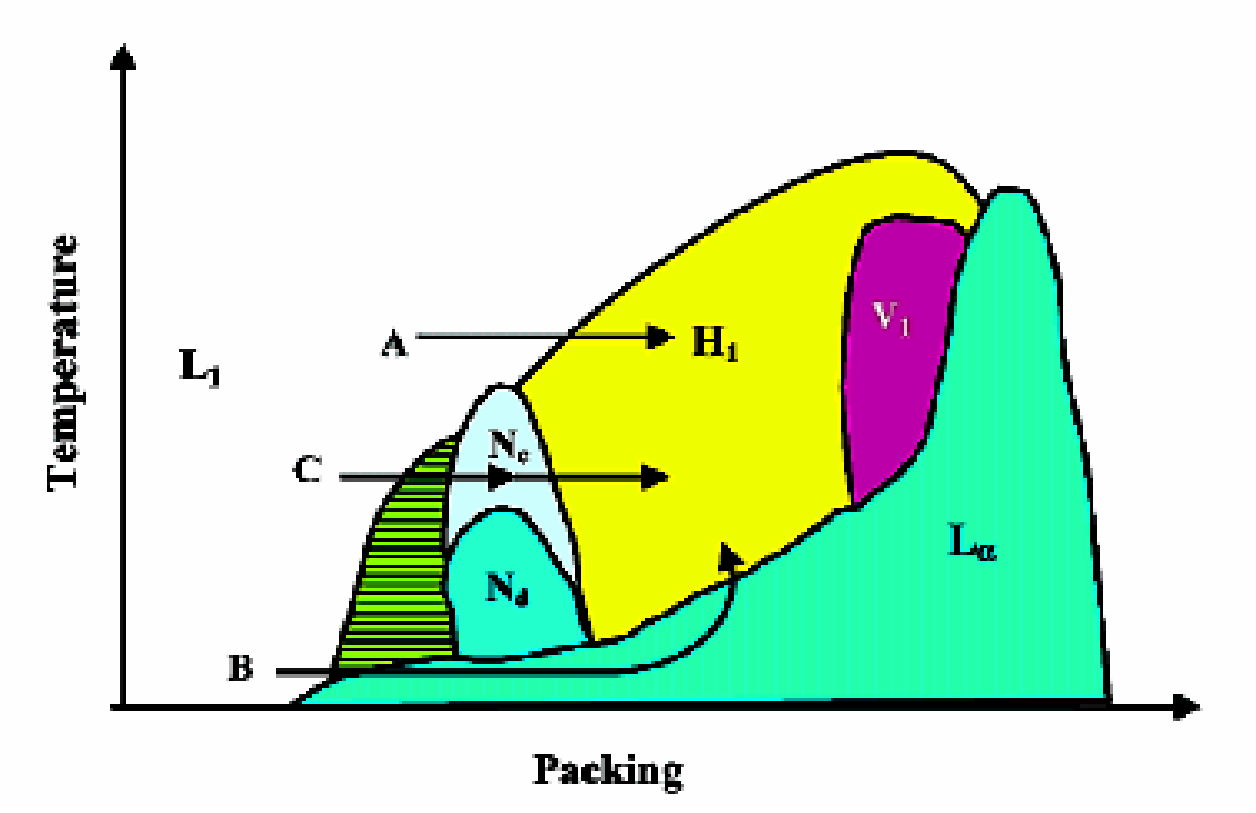
Surfactant Molecules



Conical (*icecream cone*, A) **Inverse conical (*champagne cork*, B)**

Surfactant Molecules



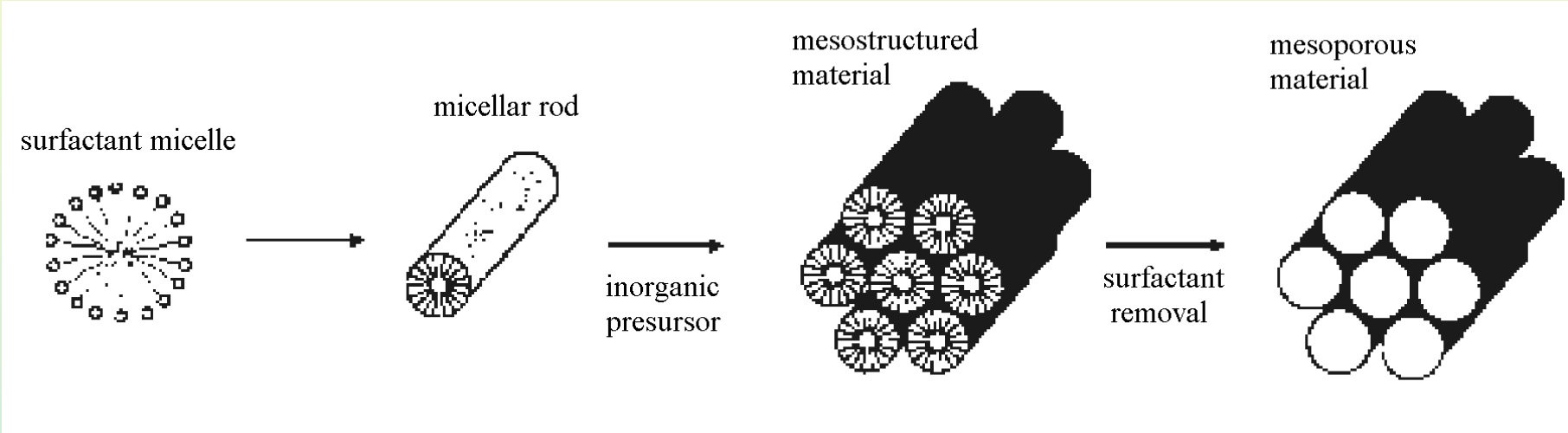


L_1= micellar solution; Nc = nematic phase; H_1 = normal hexagonal phase (MCM-41; SBA-15); V_1 = normal bicontinuous cubic phase (MCM-48); L_α = lamellar phase (MCM-50)

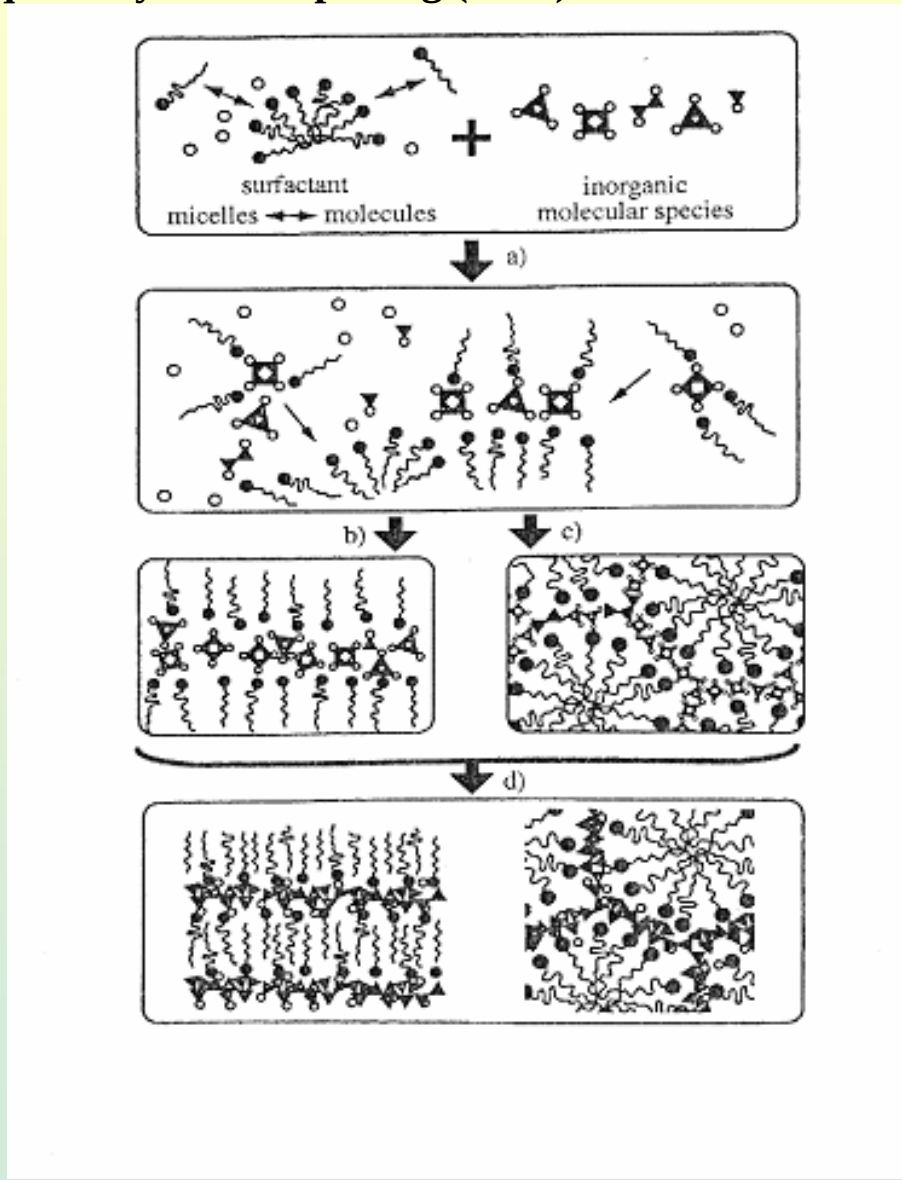
path A, the micellar solution route
path B, the lamellar phase route
path C, the nematic phase route

Mechanism of the mesoporous material formation (hexagonal, MCM-41)

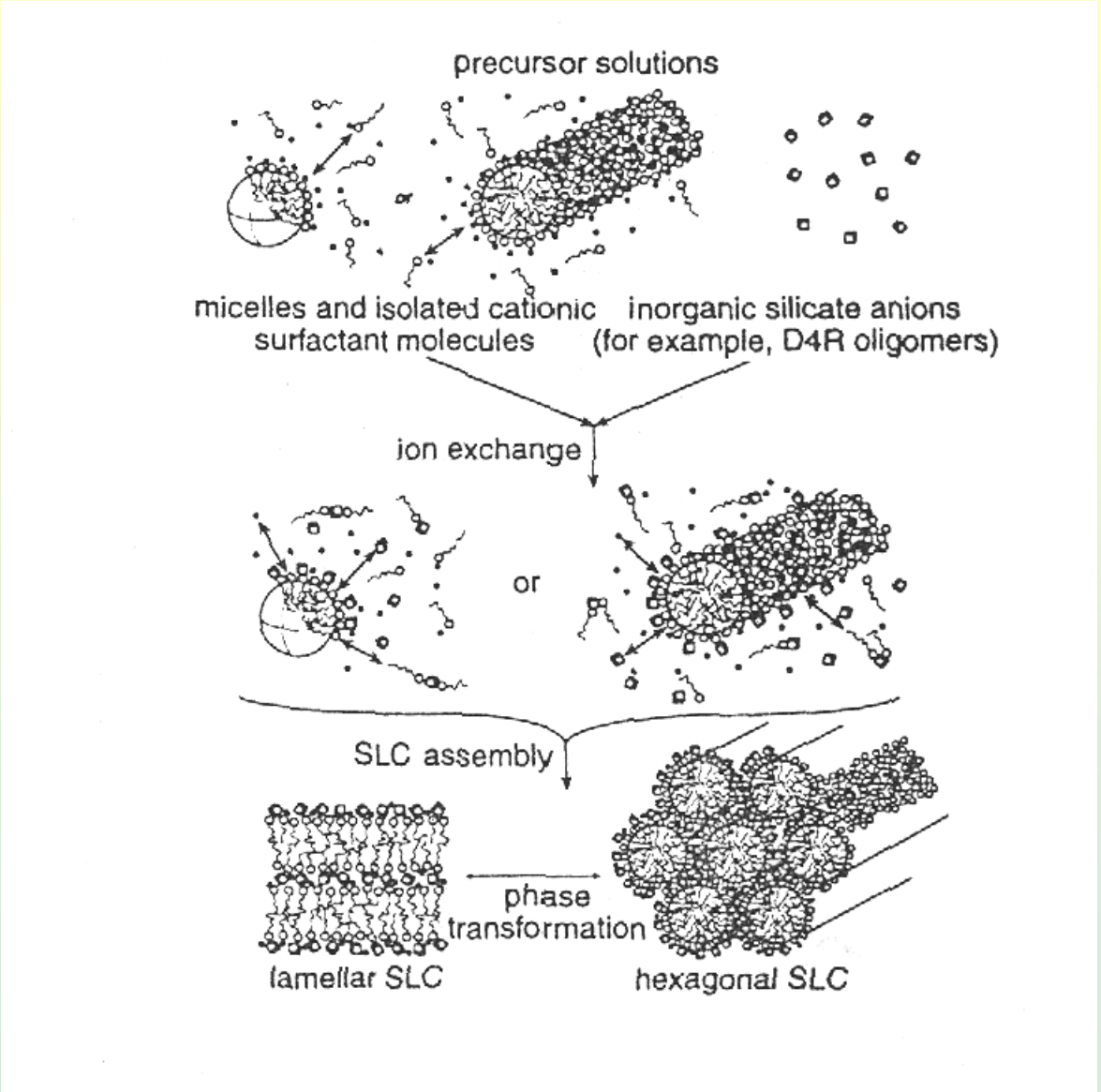
LCT Liquid Crystal Templating

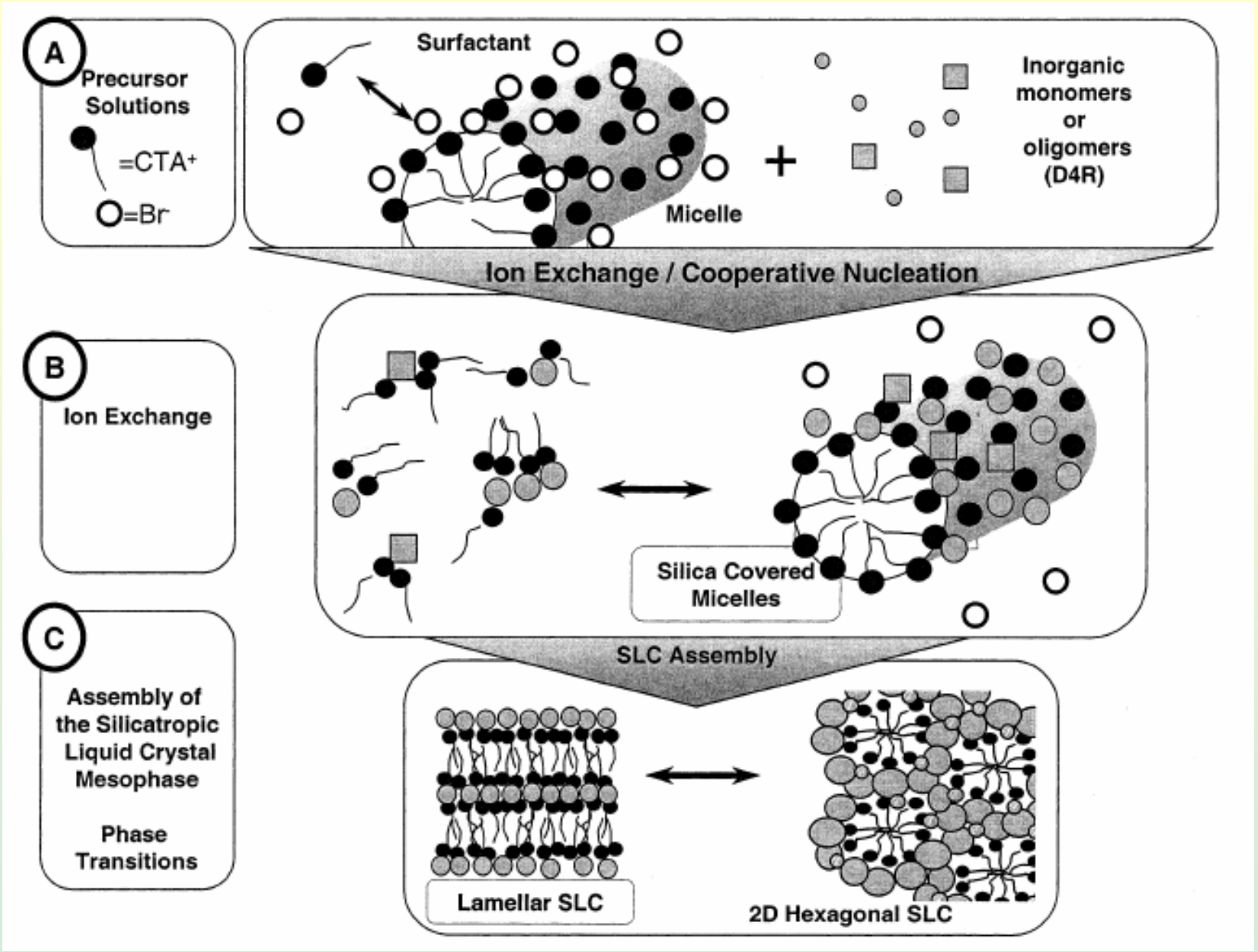


General Liquid Crystal Templating (LCT) Mechanism

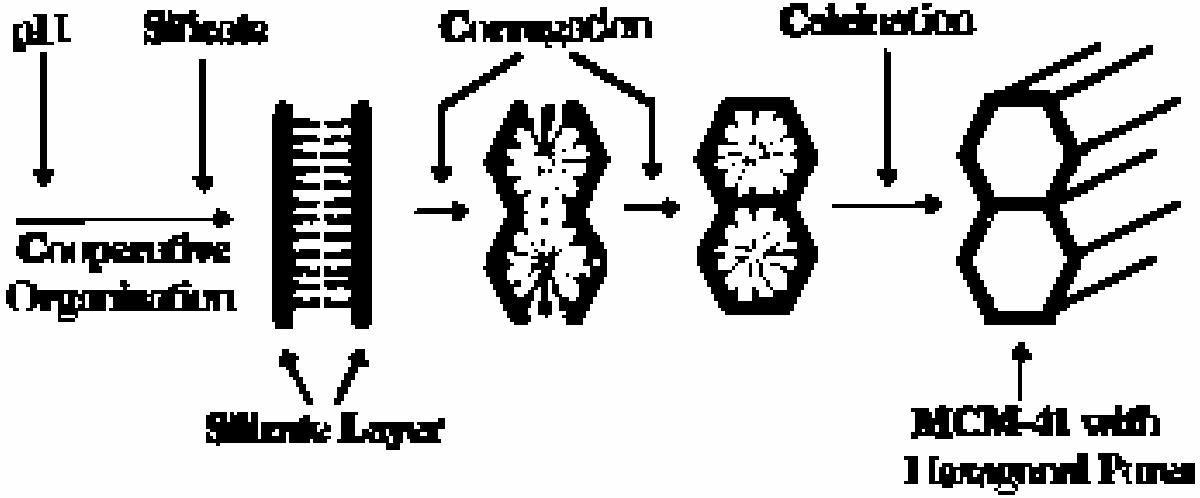


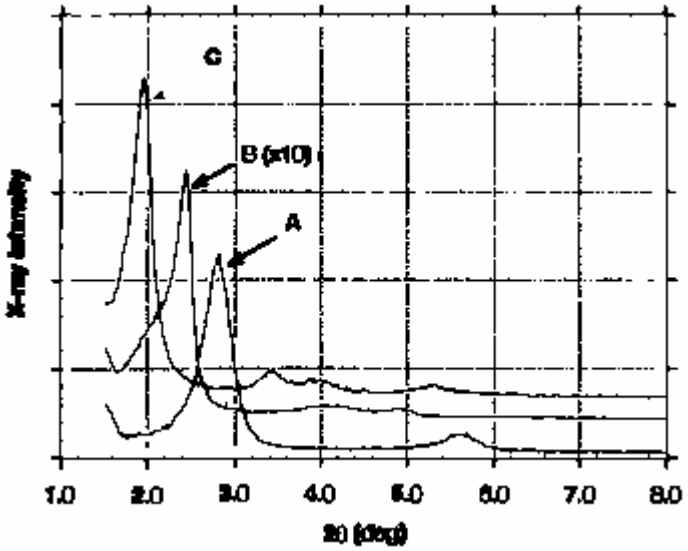
SLC Silicatropic Liquid Crystals



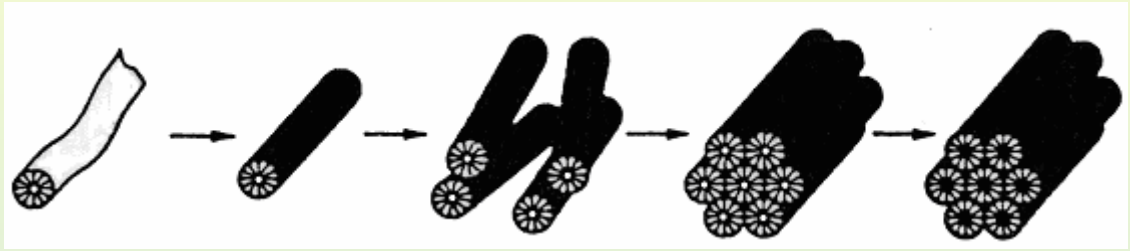

A
Precursor Solutions
=CTA+
=Br-
Surfactant
Micelle
Inorganic monomers or oligomers (D4R)
Ion Exchange / Cooperative Nucleation
B
Ion Exchange
Silica Covered Micelles
SLC Assembly
C
Assembly of the Silicatropic Liquid Crystal Mesophase
Phase Transitions
Lamellar SLC
2D Hexagonal SLC

Lamellar to Hexagonal Transformation





Silicate Rod Assembly

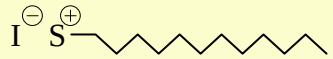


- **Electrostatic interactions**

a) $\mathbf{S^+I^-}$

I = silicate

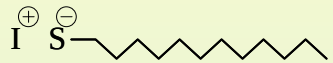
S = trimethylammonium



b) $\mathbf{S^-I^+}$

I = Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Mg^{2+}, Mn^{2+}, Pb^{2+}, Al^{3+}

S = sulfonane

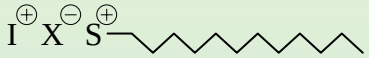


c) $\mathbf{S^+X^-I^+}$

I = silicate – polyelectrolyte positive charge

X = Cl

S = trimethylammonium

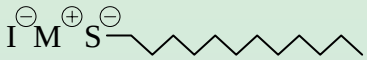


d) $\mathbf{S^-M^+I^-}$

I = aluminate

M = Na

S = phophate

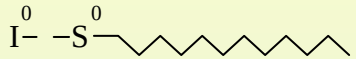


- **Hydrogen Bond**

  a) **S^0I^0**

  I = silicate

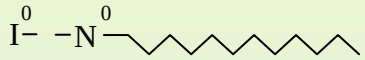
  S = ammine



  b) **N^0I^0**

  I = silicate

  N = polyethylenoxide

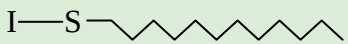


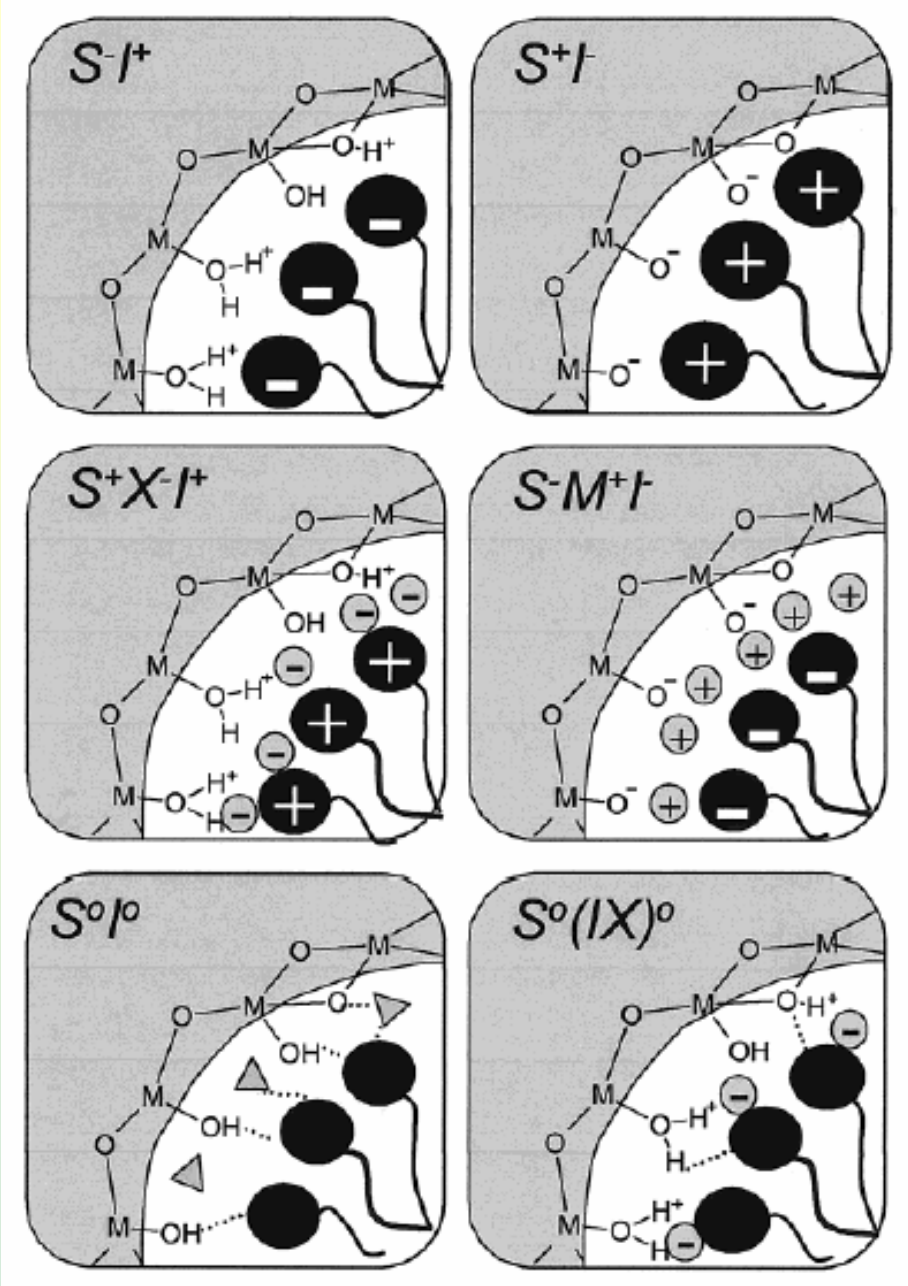
- **Covalent Bond**

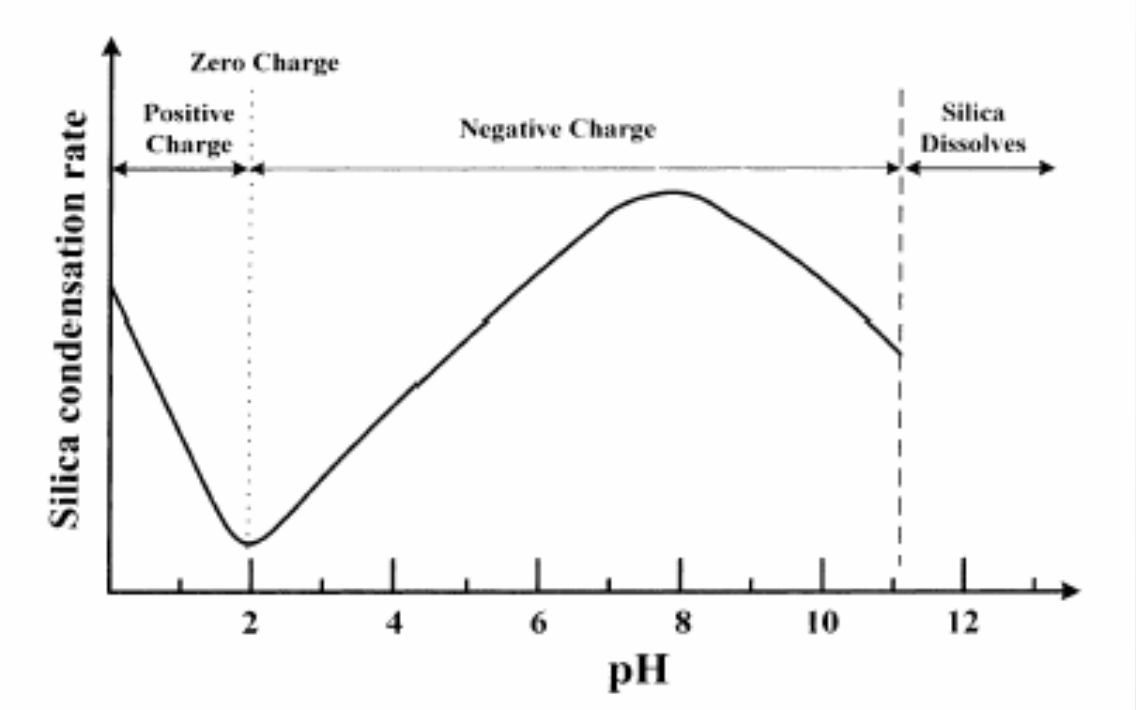
  a) **S-I**

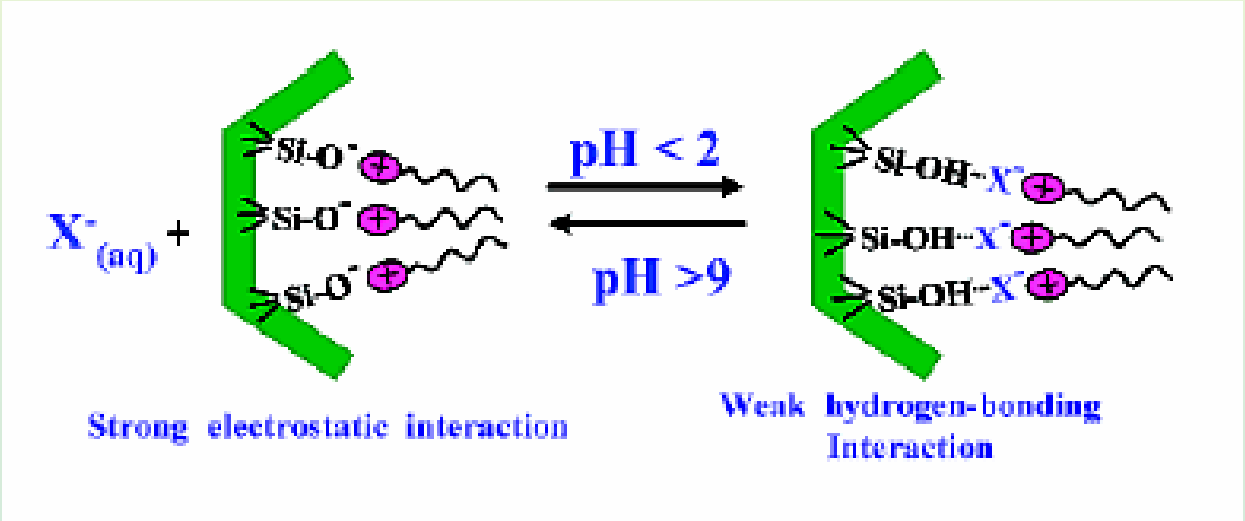
  I = niobate, tantalate

  S = ammine

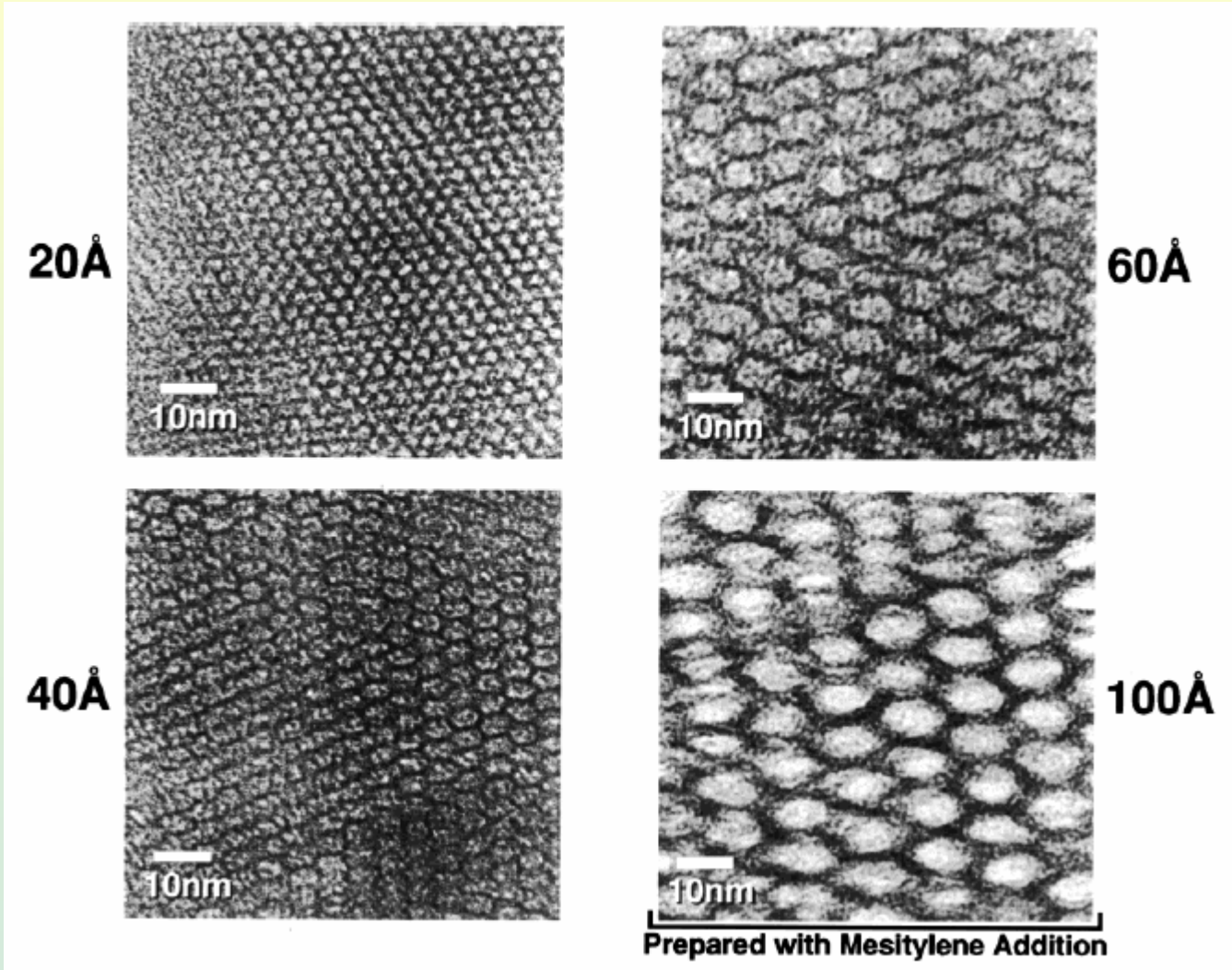



S⁻I⁺
S⁺I⁻
S⁺X⁻I⁺
S⁻M⁺I⁻
SºIº
Sº(IX)º

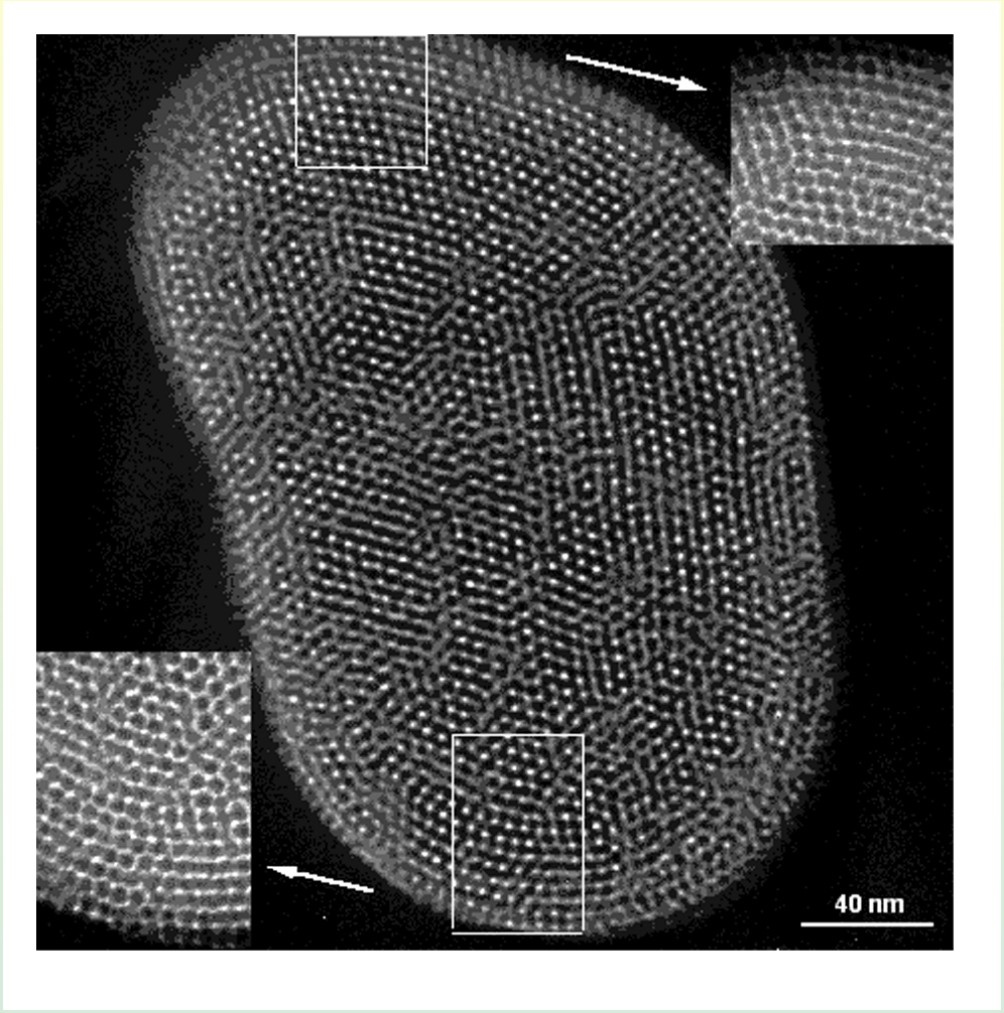

Zero Charge
Positive Charge
Negative Charge
Silica Dissolves
Silica condensation rate
2
4
6
8
10
12
pH

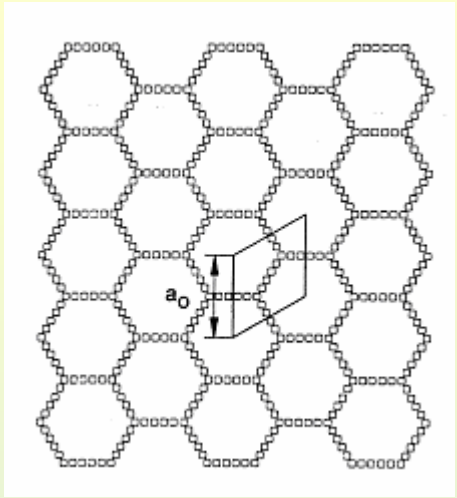

X-(aq) +
Si-O-
Si-O-
Si-O-
pH < 2
pH >9
Si-OH···X-
Si-OH···X-
Si-OH···X-
Strong electrostatic interaction
Weak hydrogen-bonding Interaction

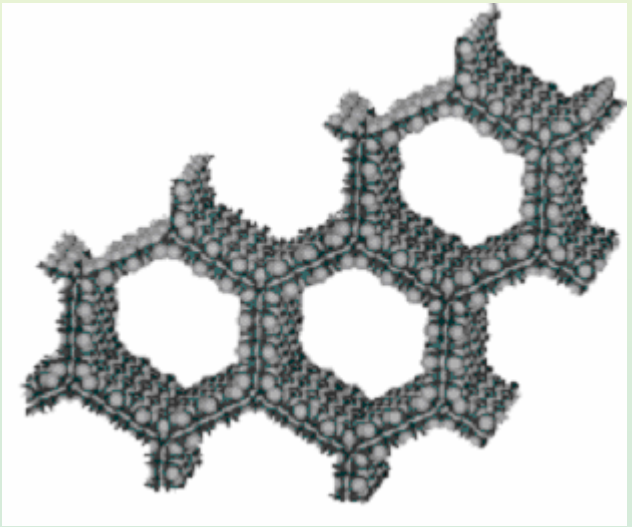
MCM-41


20Å
10nm
60Å
10nm
40Å
10nm
100Å
10nm
Prepared with Mesitylene Addition

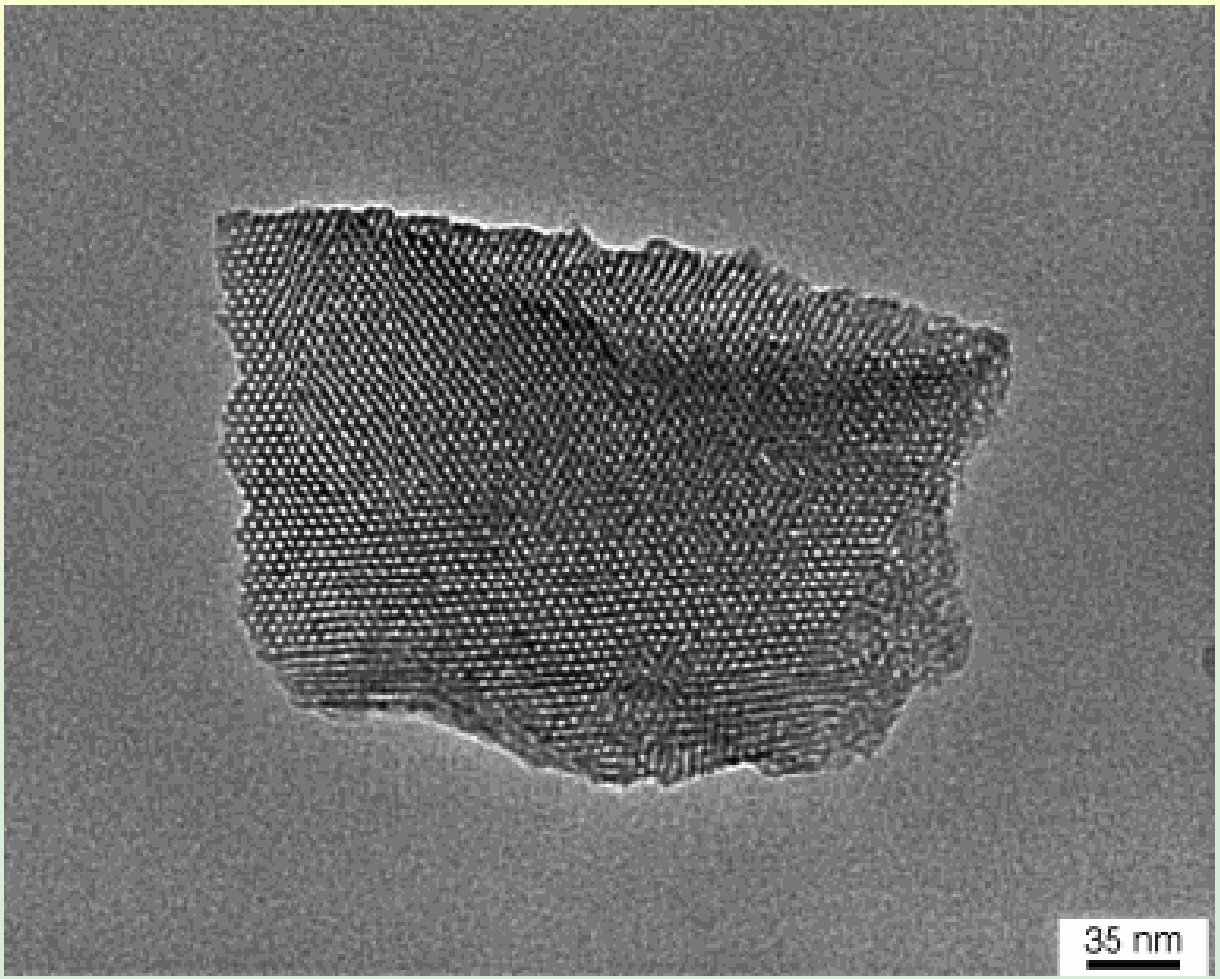
TEM micrograph of hexagonal molecular sieve



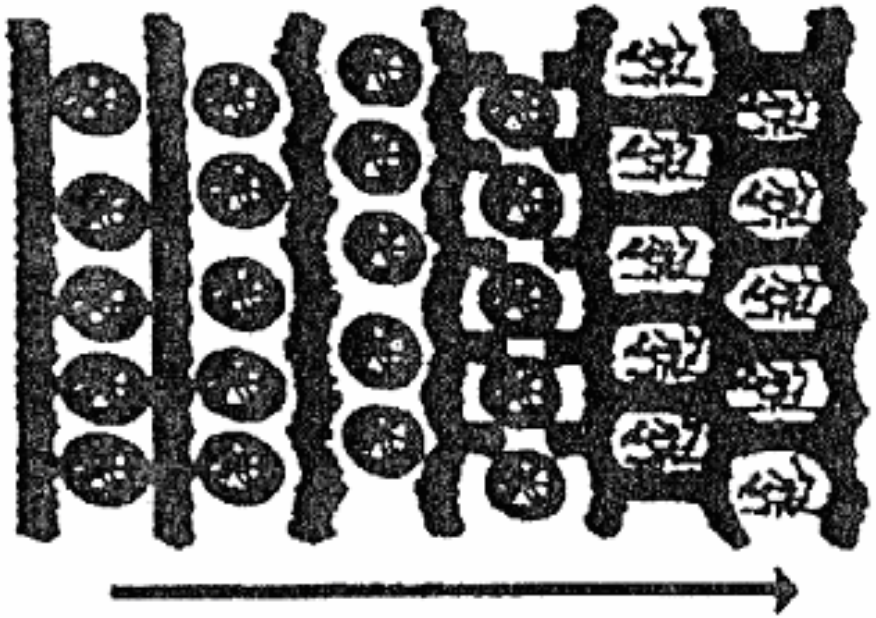




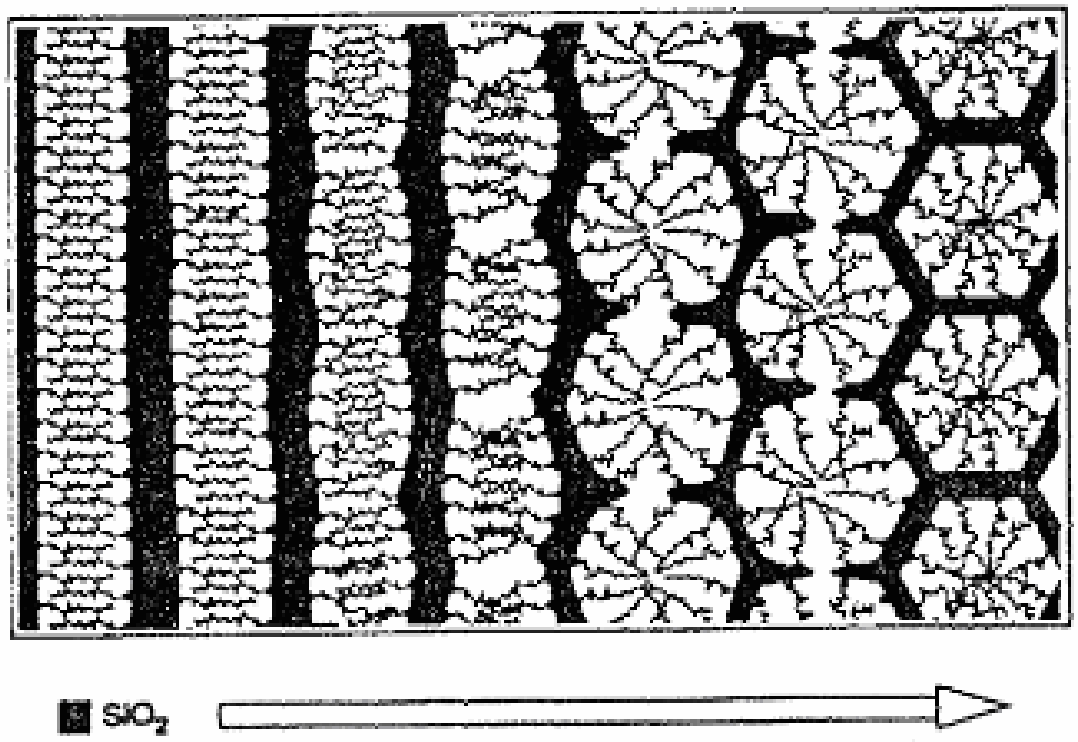
TEM image of the Pd-grafted mesoporous silicate material



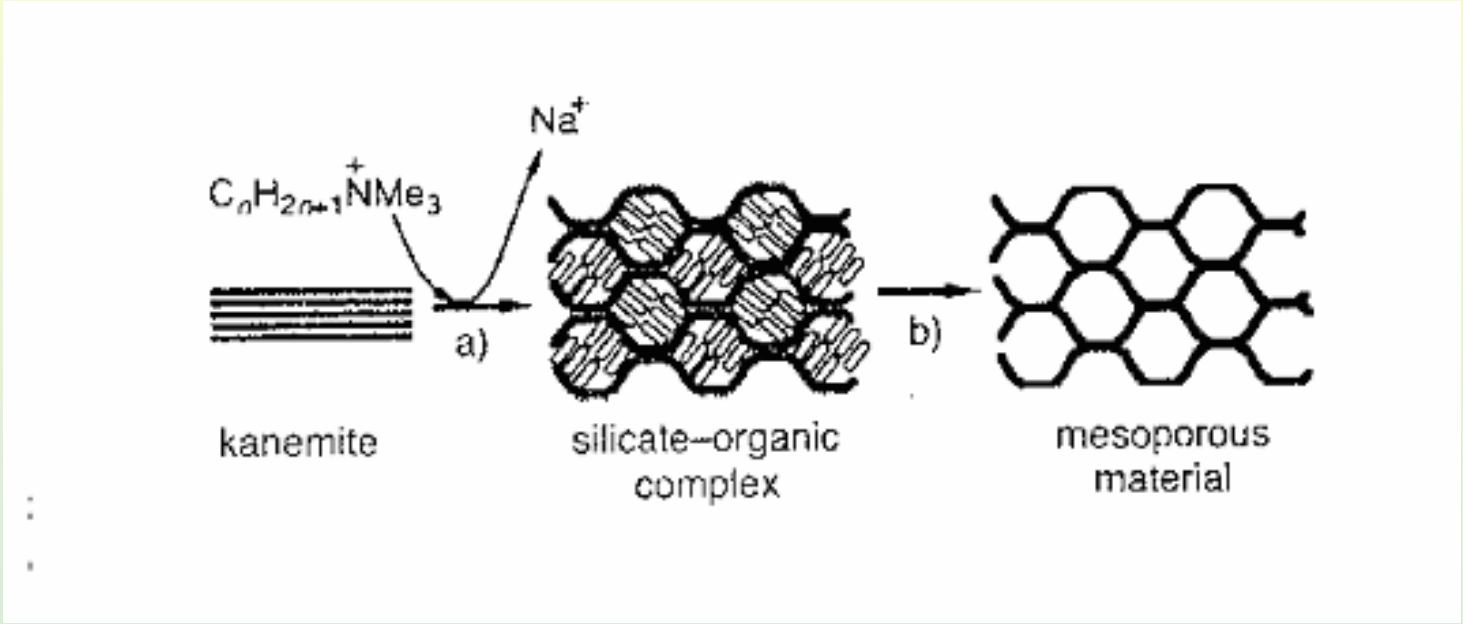
Silicate Layer Puckering



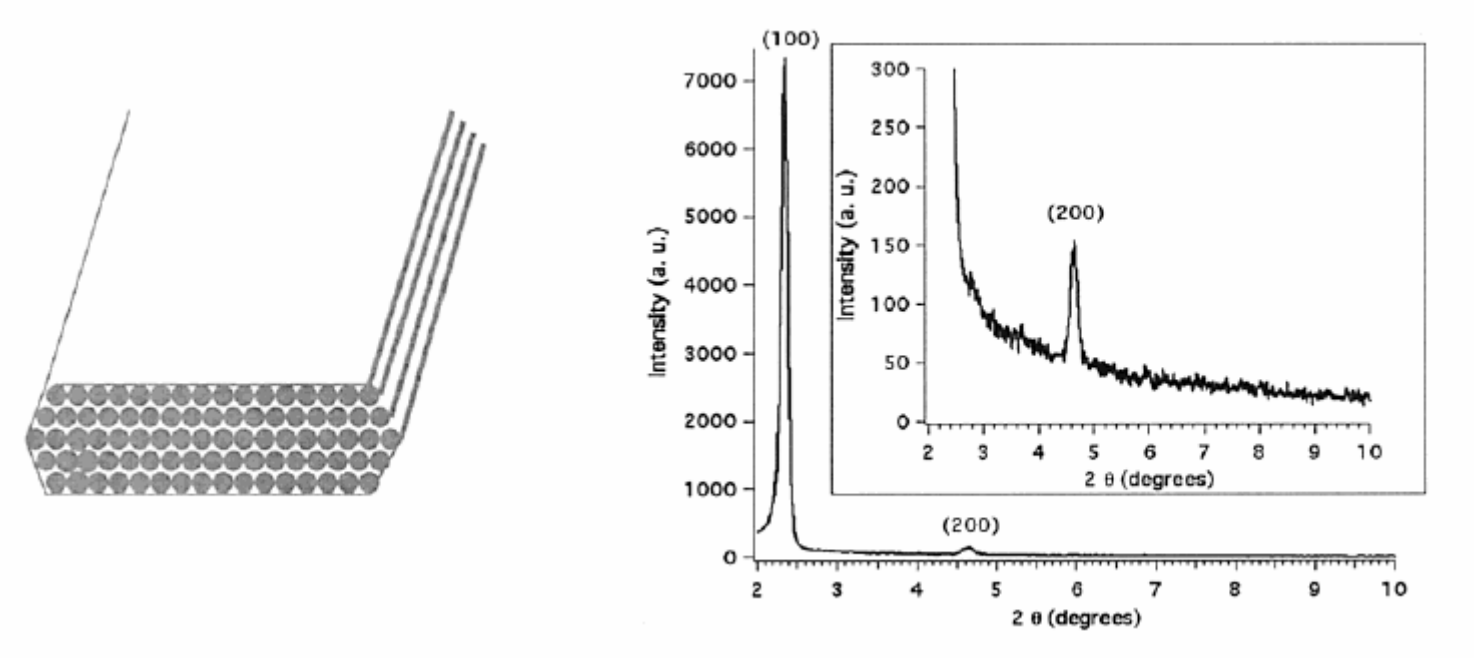
Charge Density Matching



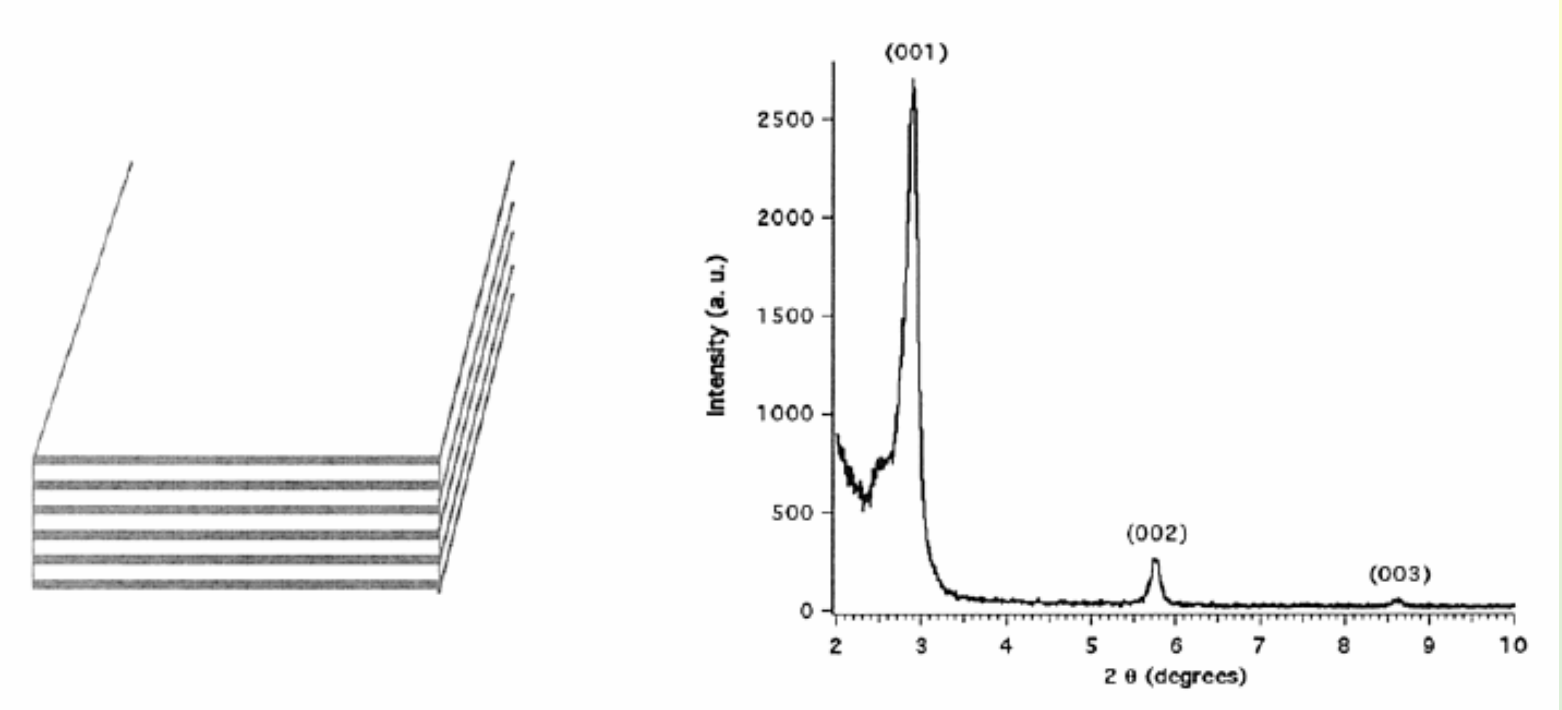
Folding Sheets

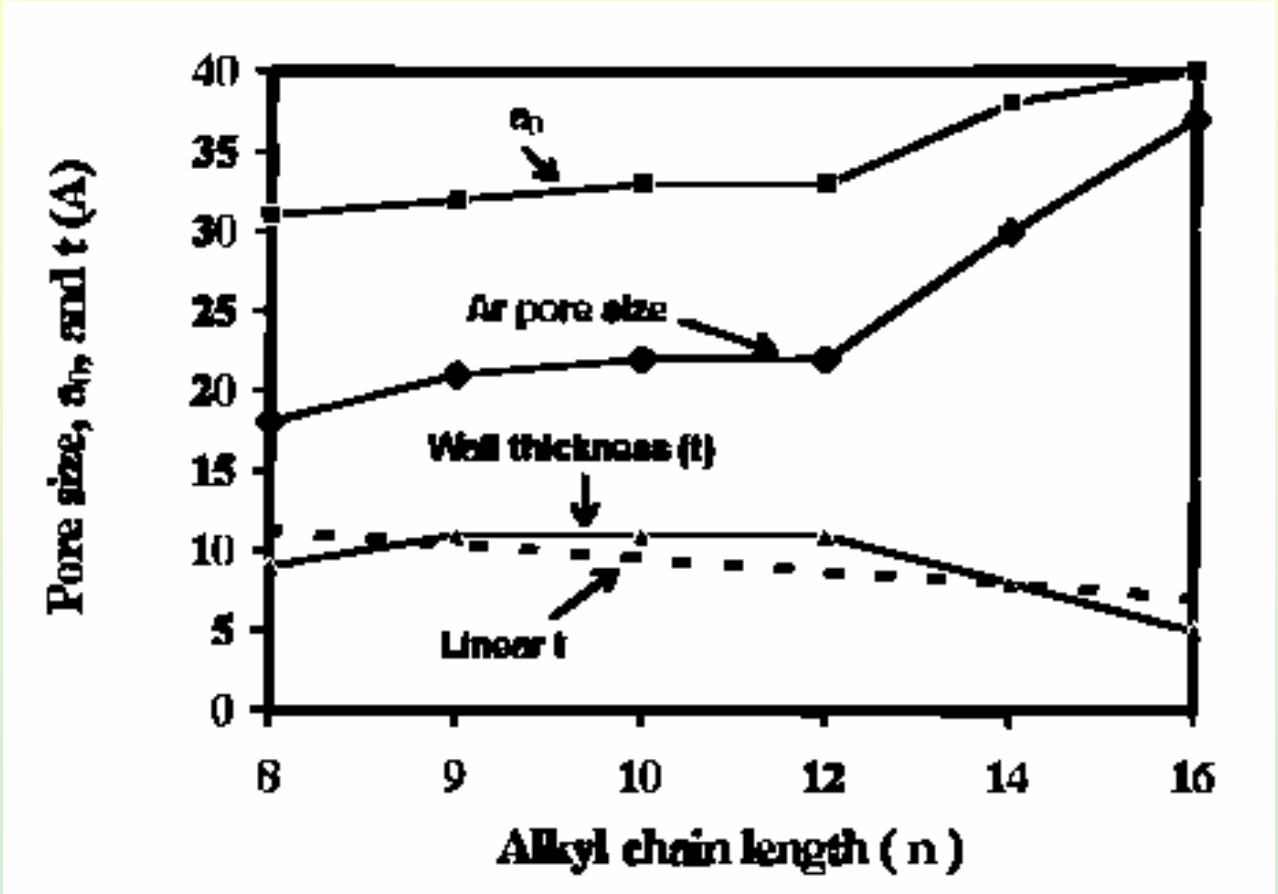


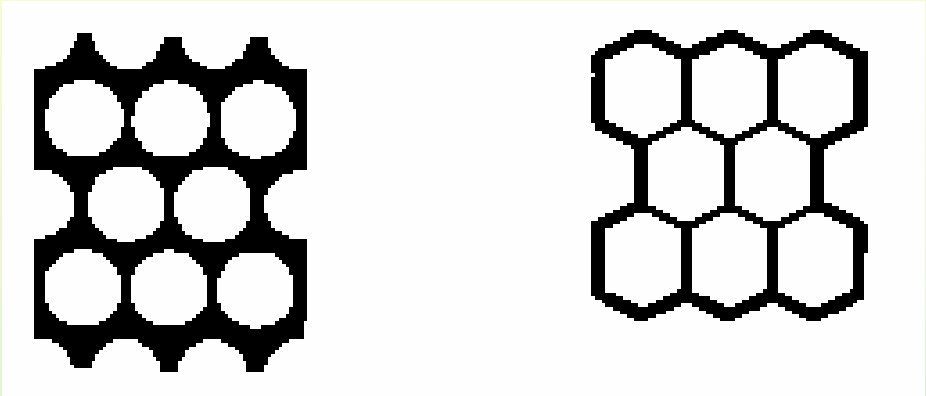
XRD of hexagonal MCM-41



XRD of lamellar MCM-50

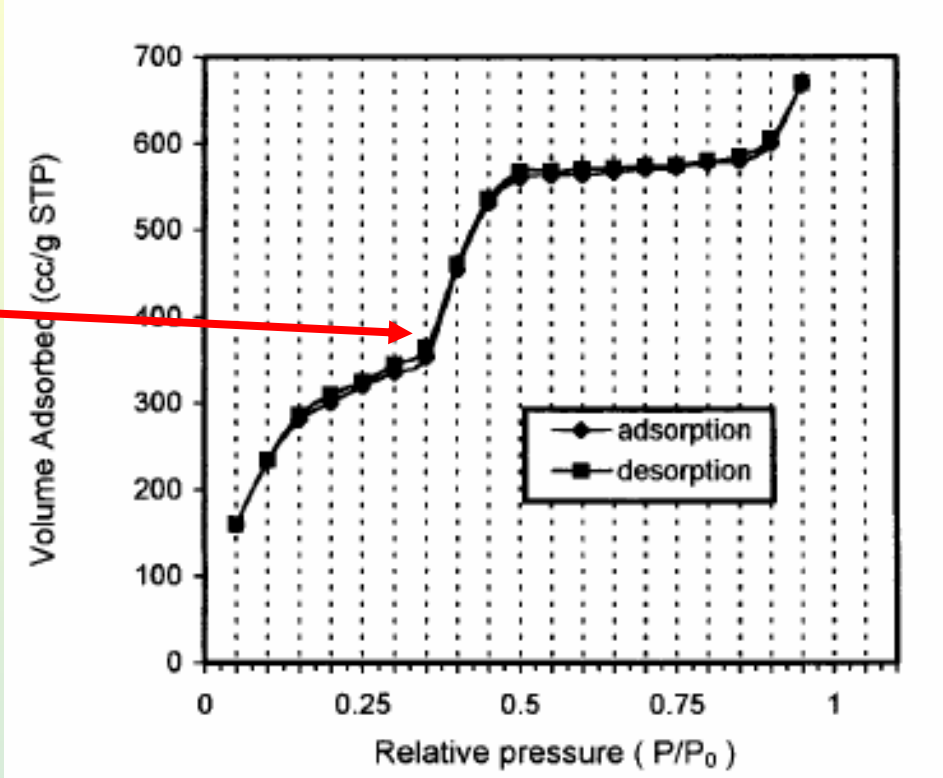



Pore size, a_n, and t (A)
40
35
30
25
20
15
10
5
0
a_n
Ar pore size
Wall thickness (t)
Linear t
8
9
10
12
14
16
Alkyl chain length (n)

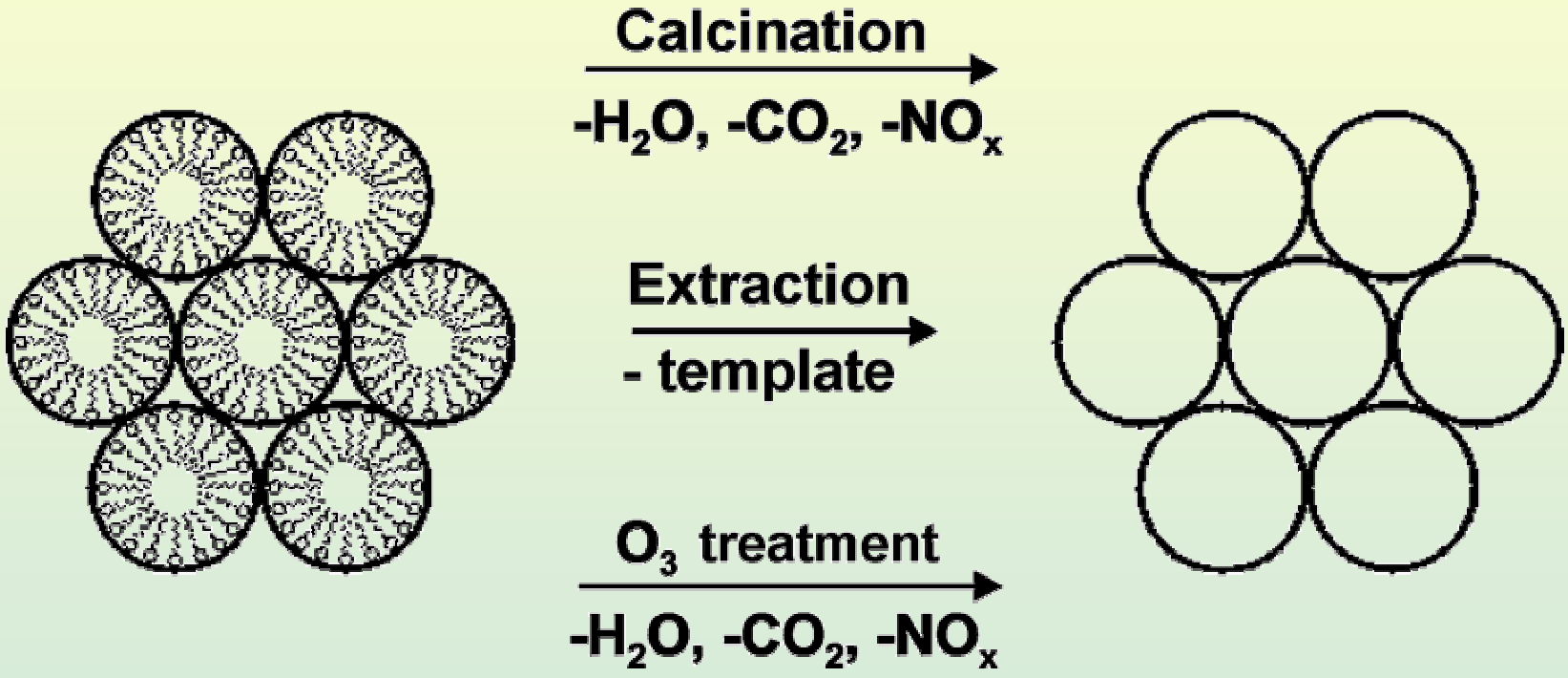


$$a_0 = \frac{2d_{100}}{\sqrt{3}}$$

Pore filling



Template Removal



Mesoporous Platinum Metal

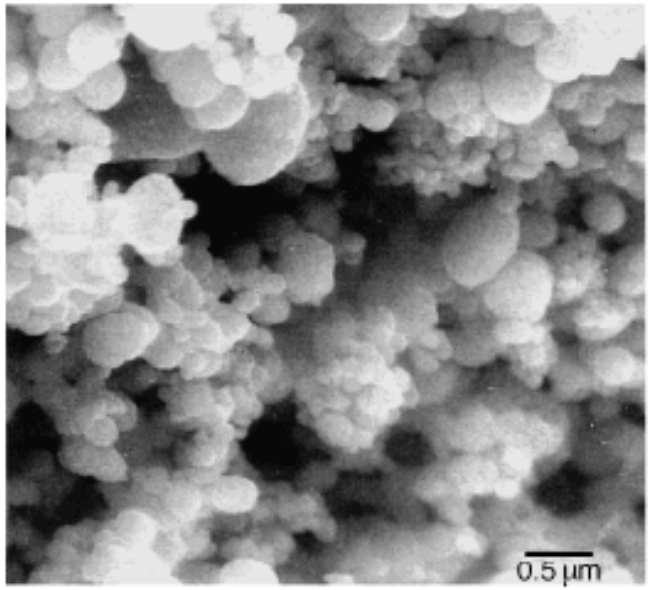
$H_2[PtCl_6]$ or $(NH_4)_2[PtCl_6]$

$C_{16}(EO)_8$

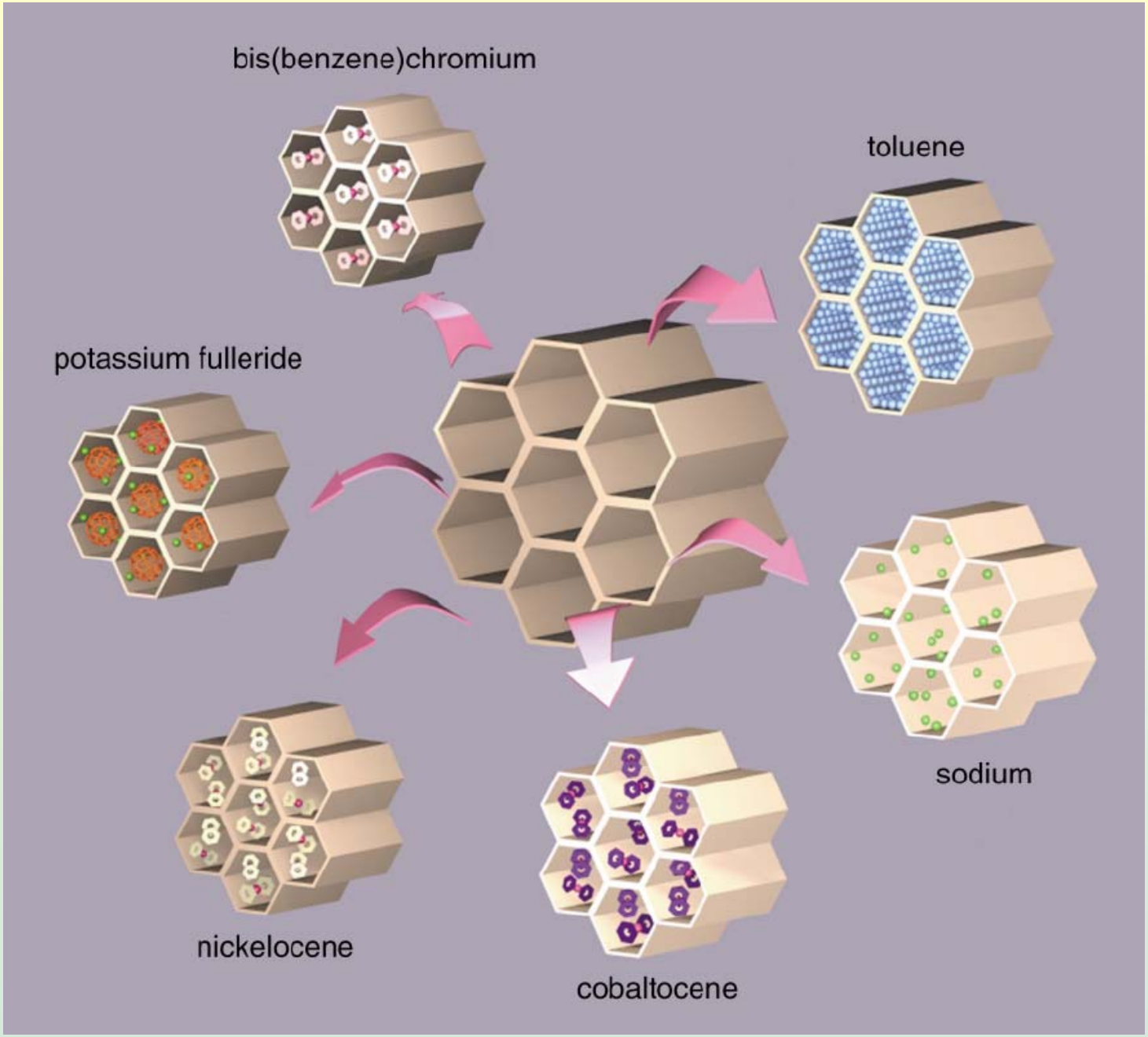
Assembly of liquid crystalline phase

Reductants: Fe, Zn, Hg, NH_2NH_2

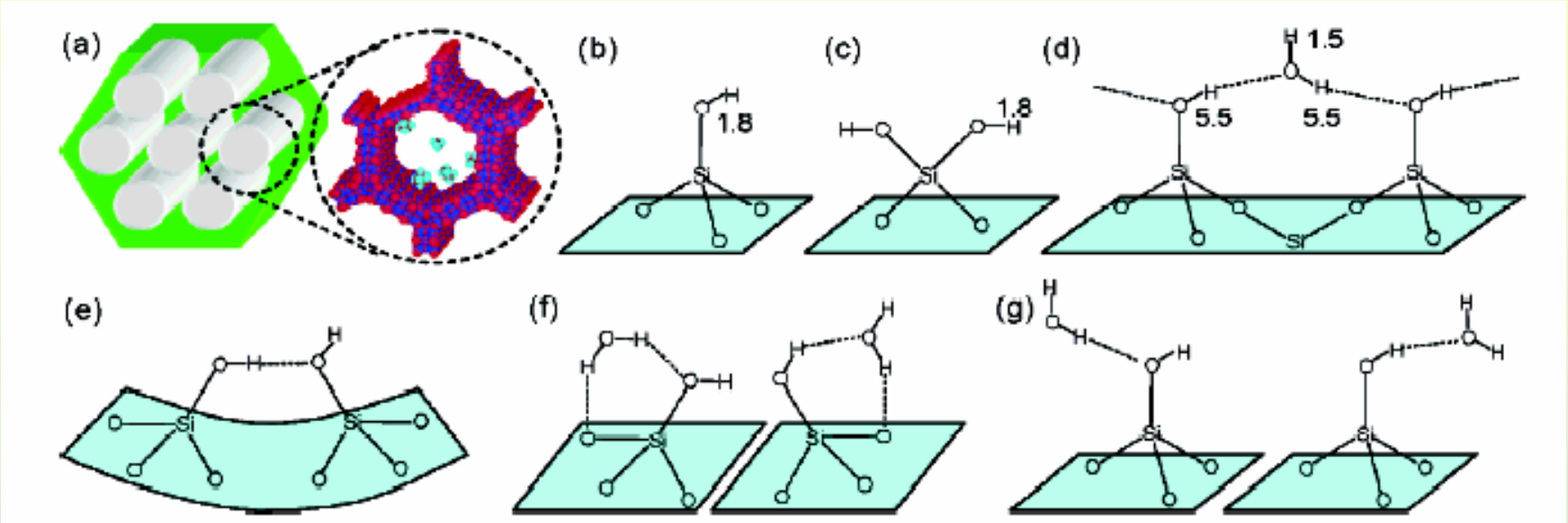
Washed with acetone, water, HCl

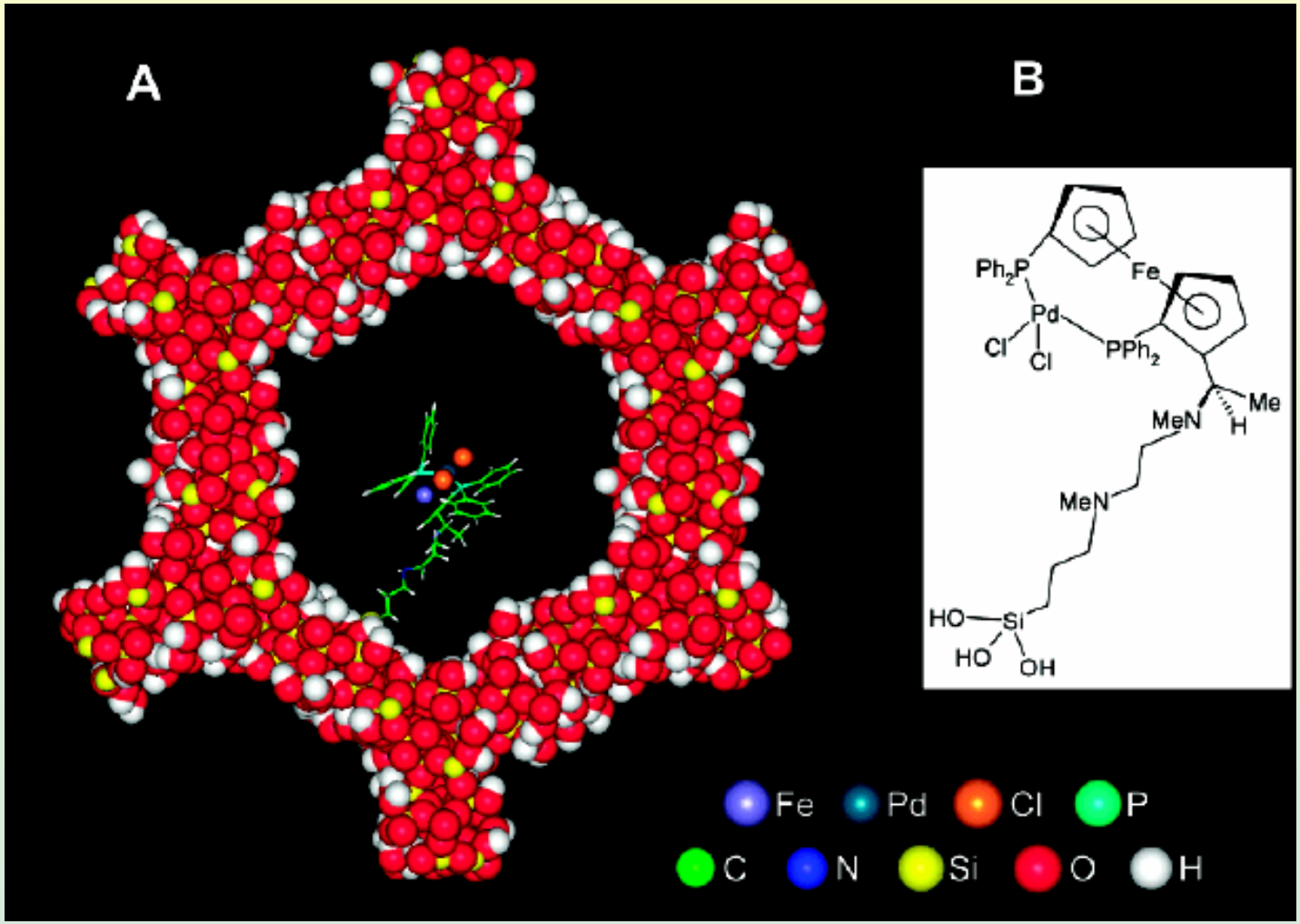


SEM (upper) and TEM (lower) images of mesoporous Pt metal show particles 90-500 nm in diameter and a pore diameter of 30 A and a pore wall thickness of 30 A.


bis(benzene)chromium
toluene
potassium fulleride
sodium
nickelocene
cobaltocene

Surface Silanols in MCM-41 Pores




A
B
Ph2P
Fe
Pd
Cl
Cl
PPh2
MeN
Me
H
MeN
HO
Si
HO
OH
Fe
Pd
Cl
P
C
N
Si
O
H